1   **BACKUP DATA - Method Nos. 7704 and 9110 / Beryllium - DRAFT**

2

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4   (Berylliant, Inc., Tucson, AZ), and Kevin Ashley (CDC/NIOSH, Cincinnati, OH)

5   Date: 28 July 2005

6

7

8   Substance: Beryllium

9

10   Exposure Limits:

11

12   Airborne Exposures:

13   OSHA: $2\mu g/m^3$; C 5 $\mu g/m^3$

14   ACGIH: $2\mu g/m^3$ (suspect Carcinogen)

15   NIOSH: Not to exceed 0.5 $\mu g/m^3$ (suspect Carcinogen)

16   (1 ppm = mg/m^3 @ NTP)

17   DOE: 10CFR850 : Airborne beryllium action level (10CFR 850.23) 0.2 $\mu g/m^3$ for 8 hour time

18   weighted average

19   OTHER/ International Standards: The UK, Sweden, Austria, France and Spain have 8-hour Be limit

20   values of 0.002 mg/m^3, while in Denmark the full-shift LV is 0.001 mg/m^3.

21

22   Surface wipes:

23   DOE :   3 $\mu g/100cm^2$ for surface contamination limit for housekeeping (10 CFR 850.30),

24   and for release of equipment (10 CFR 850.31) as 0.2 $\mu g/100cm^2$, or the concentration

25   of beryllium in the soil at the release point (whichever is higher).

26   OTHER: N/A

27

28

1.0 INTRODUCTION

29

30

31 The unique properties of beryllium (Be) have led to many applications in aerospace, the nuclear industry,

32 manufacturing, electronics, and even sports equipment. Beryllium metal is light in weight and has high

33 strength, and alloying beryllium with copper and aluminum results in materials with high corrosion

34 resistance, stiffness and low stress relaxation. Beryllium alloys are used in high-end electrical connectors,

35 springs, bearings and other components. The high thermal conductivity of beryllium oxide, while also

36 being electrically insulative, is a key component to the dissipation of heat in integrated circuits.

37 Unfortunately, beryllium is a Class A EPA carcinogen and its ingestion can cause the incurable and

38 potentially fatal lung disease, chronic beryllium disease (CBD) (1,2). Further, it has also been shown that

39 skin exposure may result in sensitization towards CBD (3). Beryllium contamination has also been found in

40 coal slag and bauxite, an aluminum ore. Thus, monitoring of beryllium in occupational environments is of

41 vital importance. Beryllium metal (as metal and as a metal alloy) and beryllium oxide are the most

42 important beryllium materials from an industrial perspective. Thus, one has to monitor and limit exposure

43 of workers in industrial workplaces to beryllium particulate matter which may be ingested via breathing or

44 may come in contact with the skin.

45

46 Current methods to detect beryllium (e.g. NIOSH 7102 and 7300) use atomic spectrometric

47 instrumentation. Preparation of samples for such analysis involves the use of highly toxic acids, and the

48 laboratory instrumentation is expensive. This instrumentation also requires highly trained personnel and is

49 not field deployable.

50

1 Sanderson, W.T., Ward, E.M., Steenland, K., Petersen, M.R., *Lung Cancer Case-Control Study of Beryllium Workers*, American Journal of Industrial Medicine, 40(3) (2001) p-284
2 Schuler, C.R., Kent, M.S., Deubner, D.C., Berakis, M.T., McCawley, M., Henneberger, P.K., Rossman, M.D., Kriess, K., *Process Related Risk of Beryllium Sensitization and Disease in a Copper-Beryllium Alloy Facility*, American Journal of Industrial Medicine, 47(3) (2005) p-195
3 Tinkle, S.S., Antonini, J.M., Rich, B.A., Roberts, J.R., Salmen, R., DePree, K., and Adkins, E.J., *Skin as a Route of Exposure and Sensitization in Chronic Beryllium Disease*, Environmental Health Perspectives, 111(9) (2003) p-1202

51   To overcome these issues, a rapid, quantitative and a sensitive test for the detection of beryllium has been

52   developed using fluorescence. The method is based on the fluorescence of beryllium bound to sulfonated

53   hydroxybenzoquinoline (HBQS), and includes a novel dissolution technique using dilute ammonium

54   bifluoride solution. The intensity of fluorescence is linear with respect to beryllium concentration. A

55   detection limit of lower than 0.02 μg Be/ 100 cm^2 has been achieved, which meets DOE regulations (4).

56   Interference studies have been carried out with a variety of metals, with minimal or no interferences found

57   for the detection of Beryllium at 100 nM in the presence 0.4 mM of the other metals. The specificity for

58   beryllium has been achieved using a number of mechanisms, such as (a) the use of ethylenediamine

59   tetraacetic acid (EDTA), which binds larger metals, (b) the use of high pH in the detection solution, which

60   causes unbound metals to precipitate, and (c) the use of HBQS, which is only able to accommodate

61   beryllium in its complexation structure. The method has been proven successful under various operating

62   conditions, including the detection of beryllium both in laboratory settings and in field trials. It fulfills the

63   requirements for a fast, inexpensive, field deployable method of detection of beryllium. Details on the

64   chemistry and development of the test method are in an attached reference from Los Alamos National

65   Laboratory (LANL) in Appendix 4.There are several advantages of the system which are summarized

66   below:

67

68   •Rapid (test results within one hour)

69   •High throughput

70   •Beryllium-specific

71   •Low capital cost (less than $10,000)

72   •Field or laboratory deployable

73   •Detection limit for wipes lower than 0.02 μg/100 cm^2

74   •Uses less hazardous solutions

75   •Uses only a fraction of material collected, an advantage for re-verification

76   •Does not require highly trained lab personnel

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4. CFR (Code of Federal Regulations), Title 10, Energy, Part 850, Department of Energy, 2001 parts 500 to end.

77

78

79   This report comprises data suitable for air monitoring and/or wipe sampling for occupational exposures to

80   beryllium. Air samples would be taken using appropriate filter media in an applicable sampler. Surface

81   wipe samples would be taken also using cellulosic wipe materials. The analytical method uses

82   fluorescence detection of beryllium using the indicator 10-hydroxybenzo[h]quinoline-7-sulfonate (10-

83   HBQS).

84

85

86   **2.0 Data Sets**

87   The data below are from different experiments having different objectives.

88

89   **2.1 Data Set 1: Analytical issues and field data (Appendix 1)***

90   The tables A1-1 to A1-12 in Appendix 1 are from Los Alamos National Laboratory (LANL), covering a

91   variety of analytical issues and evaluation of field data.

92

93   *Table A1-1:* Method detection limit data for 20x dilution

94   *Table A1-2:* Ocean Optics instrument detection limit data: HBQS test

95

96   *Table A1-3:* Recovery of beryllium from spiked Whatman 541 filters

97   *Table A1-4:* Analysis of spiked Whatman 541 filters by fluorescence and recovery confirmation of beryllium

98   using 1% ammonium bifluoride solution

99   *Table A1-5:* Analysis of spiked Whatman 541 filters by fluorescence

100   *Table A1-6:* Analysis of spiked MCE filters by fluorescence

101   *Table A1-7:* Interference Study – To look into interference caused by other elements

102   *Table A1-8:* Long term experiment to determine aging of samples

103   *Table A1-9:* Long term experiment to determine stability of detector (with HBQS dye) solution.

104   *Table A1-10:* Field data from a LANL machine shop- comparison with ICP

105   *Table A1-11:* Field data from a LANL firing range- comparison with ICP and recovery of beryllium from

106   Whatman 541 using 1% ammonium bifluoride.

107   * In many of these tables the procedures that were followed are given in *NIOSH Technical Report,*

108   *Guidelines for air sampling, analytical method development and evaluation, 1995, Publication 95-117.*

109   Page numbers from this report are listed in individual tables.

110

111

112   In many of these tables, concentration of beryllium in the measurement solution (in units of parts per

113   billion, ppb) is related to the quantity of beryllium on the media (e.g., filter paper) in units of μg. For

114   sample preparation where 20X dilution is used, one starts out with 5ml of dissolution solution (I%

115   ammonium bifluoride) to dissolute the beryllium on the media. Of this, 0.1ml of the dissolution solution is

116   added to 1.9ml of the dye solution (20X dilution) for measurement. The "Standard Solutions" used for

117   calibration have beryllium concentration measured in ppb. The table below shows typical standards used

118   and how the beryllium concentration in the solution in ppb correlates to the amount of beryllium in μg on

119   the media

120

Preparation of Standard Solutions	Concentration of beryllium (ppb) in cuvets comprising calibration standards and detector solution	Comments
0.1 ml of **0 ppb standard +** 1.9 ml of detection solution	0.0	Corresponds to 0.00 μg beryllium on media
0.1 ml of **10 ppb standard +** 1.9 ml of detection solution	0.5	Corresponds to 0.05 μg beryllium on media
0.1 ml of **40 ppb standard +** 1.9 ml of detection solution	2.0	Corresponds to 0.2 μg beryllium on media
0.1 ml of **200 ppb standard**	10.0	Corresponds to 1 μg

+ 1.9 ml of detection solution	.	beryllium on media
0.1 ml of **800 ppb standard**	40.0	Corresponds to 4 µg
+ 1.9 ml of detection solution		beryllium on media

121

122

123   All data in this report were taken at 20x dilution, which means that the volumetric ratio of the sample

124   solution (in dissolution solution) to the detection solution was 1:19. Mechanical agitation was used for

125   obtaining all of these results, which was carried out by rotating the sample tube for 30 minutes. All of

126   these data were generated using an Ocean Optics Fluorometer unless reported otherwise in these tables.

127   For more details on instrument settings and other instruments, please see section 2.4 below (and within

128   these tables).

129

130   Tables A1-3 and A1-4 show supportive data on the effectiveness of using 1%ammonium bifluoride as

131   dissolution solution. The results show that this solution and the method used is highly effective. Table A1-5

132   shows results from different lots of Whatman 541 filters. Different filter lots may have differing amounts of

133   residual acid. The results show that all lots gave identical results.

134

135

136   **2.2 Data Set 2: Evaluation of ammonium bifluoride extraction of various compounds of beryllium**

137   **and various sampling media (Appendix 2)**

138   These experiments were conducted at NIOSH. The fluorometer used in this experiment was from Ocean

139   Optics. The purpose of this experiment was to evaluate if 1% ammonium bifluoride was suitable in

140   extracting non-water-soluble beryllium compounds such as BeO and water-soluble compounds such as

141   beryllium sulfate obtained from Sigma-Aldrich Co. According to a specialist from Sigma Aldrich, beryllium

142   oxide powders supplied by them are processed at 2000 °C ("High Fired"). The ammonium bifluoride was

143   found suitable for dissolution of beryllium compounds. The dissolution solution was agitated mechanically

144   and ultrasonically and both methods were found suitable.

145   The wipe results indicate that Ghost wipes were not suitable. Furthermore, some batches of Ghost wipes

6

146   have been found to be contaminated with beryllium[5]

147

148

149   **2.3 Data Set 3: Comparison of dissolution methods using a difficult to solubilize commercial**

150   **beryllium oxide material (Appendix 3)**

151   These experiments were conducted at LANL using UOX125 BeO (obtained from Brush Wellman and

152   considered "High Fired"). The purpose of the experiment was to investigate the applicability of the method

153   on a commercial BeO powder, and also to evaluate different methods of dissolution using 1% ammonium

154   bifluoride. Slurries of these powders were prepared and Whatman 541 filters were spiked with BeO. The

155   method used to prepare this slurry is given in Appendix 7. These samples were then extracted using 1%

156   ammonium bifluoride using mechanical agitation (which is done at room temperature), and also by heating

157   the solutions to 75, 80 and 90 °C without mechanical agitation. Aliquots from these samples were then

158   analyzed using a Turner-Quantech fluorometer and by ICP-AES. These results are shown in Appendix 3.

159   This data shows that when heating is used 1%ammonium bifluoride dissolution is as effective as acid

160   dissolution protocols used in ICP analysis. The results also show that if the amount of beryllium oxide

161   present on the sampling medium is up to the regulation limit of 0. 2 µg, then either mechanical agitation or

162   heating may be used. If beryllium oxide is present in higher quantities, then heating at or in excess of 75

163   °C is recommended. However, it was concluded that mechanical agitation using 1% ammonium bifluoride

164   is sufficient to raise a "red flag" in case the difficult to solubilize beryllium oxide is present anywhere near

165   the regulation limit.

166

167   **2.4 Data Set 4: Interlaboratory agreement (Appendix 5)**

168   The purpose of this experiment was to check for interlaboratory consistency on filters (Whatman 541 and

169   mixed cellulose ester (MCE) filters) spiked with pre-determined amounts of beryllium. The amount of

170   beryllium on the filters was not revealed to the labs that conducted the analyses. All labs used 1%

171   ammonium bifluoride for extracting beryllium, and a dye detection solution supplied by a single source, but

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5. Private communication with NIOSH and discussions within Beryllium Health and Safety Committee

172 used different fluorescence instruments to analyze the samples: The experimental details and the results

173 are shown in Appendix 5, and the instruments used, along with important parameters, are listed below.

174

175 The Fluorometers which have been found suitable for this method are: (1) Turner Quantech FM109515

176 from Barnstead Thermolyne (Dubuque, Iowa); (b) RF1501 from Shimadzu (Columbia, Maryland); (c)

177 USB2000-FLG from Ocean Optics (Dunedin, Fl); and (d) SPEX Fluorolog 2 (Horiba, Irvine, CA).

178

179 Parameters used for Turner Quantech: Excitation band-pass filter with peak transmission at 360 nm and

180 bandpass of 40 nm (NB360 part# from Barnstead LE1095X30). Emission band-pass filter with a peak

181 transmission at 460 nm with a bandpass of 10 nm (NB460 part# from Barnstead LE1095X12). Small

182 volume position of sample holder was used. Autogain parameter was used.

183

184 Parameters for Shimadzu RF1501: Excitation at 360 nm, emission at 475 nm (bandpass was ±10 nm for

185 both).

186

187 For the Ocean Optics instrument an LED with peak emission at 380 nm was used (LED380), and the

188 emission was integrated at 475 nm; a 1 mm diameter fiber optic cable (part # P1000-2-UV-Vis) was used

189 to connect the sample holder and the spectrometer. .

190

191 A SPEX Fluorolog 2 instrument, made by Jobin-Yvon SPEX (now Horiba), was also used. The excitation

192 wavelength was 380 nm and the emission wavelength was 475 nm. In both cases the bandpass was 5 nm

193 and integration time was 1 second. The light source was a 450 W Xenon arc lamp.

194

195 Data from this study was statistically analyzed for bias and repeatability and reproducibility. These results

196 are discussed and explained in **Appendix 5** and the results tabulated in **Appendix 6**.

197

198 **3.0 Source of Reagents and Solutions**

199

200   1. Spiked filters for perfomance evaluation material samples (PEMs) by inter-laboratory testing were

201   prepared by spiking with beryllium nitrate in deionized water. Both type of filters, i.e., Whatman

202   541 and mixed cellulose ester (MCE) were spiked. Whatmans and MCEs are, respectively, used

203   for surface sampling and for collecting particulate matter by air sampling.

204   2. Sources of beryllium oxide were Acros Chemicals (99%), Sigma-Aldrich Chemical Company

205   (99.98%) and Brush Wellman for UOX125. See Appendix 3, 4 and 5 for details on which kind of

206   beryllium oxide was used in specific tests. Sources of beryllium sulfate were Acros and Sigma-

207   Aldrich.

208

209

210   **4.0 Analytical Aspects**

211

212   In all data sets the dissolution solution was 1% ammonium bifluoride in deionized (DI) water (w/w). The

213   detection reagent was prepared by the addition of 12.5 mL of 10.7 mM EDTA and 25 mL of 107 mM L-

214   lysine monohydrochloride to 3 mL of 1.1 mM 10-HBQS (10-hydroxybenzo[h]quinoline-7-sulfonate). The pH

215   was adjusted to 12.85 with the careful addition of 10 M NaOH, and water was added to achieve a total

216   volume of 50 mL.

217

218   The reagents used in the Inter-laboratory testing in Data Set 4 were purchased from Fisher Scientific

219   (Pittsburgh, PA), with the exception of 10-HBQS, which was synthesized in the laboratory.

220

221   This method is not restricted to a particular type of fluorometer. As long as good calibration is obtained

222   (correlation coefficient of equal or greater than 0.99) using the standards within and close to the regulation

223   range, any fluorometer may be used. The list below includes fluorometers used successfully in the various

224   data sets generated.

225

226   As stated above, the fluorometers which have been found suitable for this method are Turner Quantech

227   FM109515 from Barnstead Thermolyne (Dubuque, Iowa), RF1501 from Shimadzu (Columbia, Maryland)

228 and USB2000-FLG from Ocean Optics (Dunedin, Fl). The instrument parameters found suitable are

229 discussed above in section 2.4.

230

231

232 **4.1 Sampling Aspects**

233

234 This test is on the analytical aspects of the media with beryllium particulates, and not on the sampling

235 issues. Sampling studies were not undertaken.

236

237

238 **4.2 Dissolution Efficiency**

239

240 Recovery of sample during dissolution was not an issue in the materials examined so far, nor in the

241 concentrations used which span the regulation requirements. This can be seen in Tables A1-3, A1-4, A1-

242 5, A1-6, A1-10, A1-11 of Appendix 1, Table A2-1in Appendix 2 (with the exception of Ghost Wipes) and

243 UOX125 BeO in Table A3-1 and Table A3-2 in Appendix 3. Heating during dissolution is particularly

244 preferred when high fired BeO (e.g., UOX 125) is present in excess of $0.2\mu g$ in the media. From these

245 data on UOX125 it is preferable to dissolute high fired BeO by heating ammonium bifluoride in the range

246 of 75 and 90°C.

247

248 This method was developed for use in the analysis of beryllium by sampling of air or surfaces. The

249 volumes for time-weighted average (TWA) or short-term exposure limit (STEL) air samples are expected

250 to be the same as were used in the development of NIOSH 7102 and NIOSH 7300.

251 Dynamically generated test atmospheres were not created as this is a difficult experiment to conduct from

252 a safety perspective; however, these issues are not expected to be any different as compared to NIOSH

253 7102 or NIOSH 7300. Breakthrough studies and sampling in humidity were not tested with this method.

254

255 For the development of the sampling methods, different procedures were used to generate the

256 performance evaluation samples. These included spiking of Whatman 541 and MCE filters by beryllium-

257 soluble compounds in water, slurries of oxides, and wipe samples collected from the field. Please see

258 details in various data sets (appendices) for more information.

259

260

261

262 Please see Table A1-4 (appendix 1) for the data used in determining the precision and bias at for

263 beryllium. A calibration curve was done using 6 levels of beryllium with 6 replicates at each level over the

264 range of 0.02 to 3.00 µg/sample. The calibration curve gave a calculated NIOSH method accuracy of

265 14.4% at the upper 95% confidence limit, a precision of 4% relative standard deviation (RSD), and an

266 estimated bias of -0.0088. These calculations were done using the formulas in Chapter 0 of the NMAM[6].

267 The NIOSH Guidelines for Air Sampling and Analytical Method Development and Evaluation calls for the

268 method accuracy to be within ± 25% of the true concentration.

269 **4.3 Determination of sampling and analytical LOD and LOQ**

270

271 The data for calculating limit of detection for the method and the instrument is shown in Appendix 1 as

272 Tables A1-1 and A1-2. Since a detection limit of 0.02µg is required (for detecting an exposure limit of

273 0.2µg), we assumed this being the limit and designed a test with five samples at 0.02µg, one at 0.1µg (5X)

274 and five at 0.2µg (10X) according to NIOSH procedures as explained in Appendix 4 (see section on

275 detection limit). When this data was fitted, we obtained a detection limit of 0.0136µg (or 13.6ng/filter

276 paper).

277

278 Similarly to evaluate the Ocean Optics Instrument detection limit we assumed a number of 0.006µg as the

279 detection limit, which following a similar experimentation and analysis as above resulted in the instrument

---

6. E.R. Kennedy, T.J. Fishbach, R. Song, T.M. Eller, SA Schulman, NIOSH, CDC, May 1995. US Government publication number: DHHS (NIOSH) 95-117.

280   detection limit of 4.15ng/filter.

281

282

283   **4.4 Storage Stability**

284

285   Since beryllium and beryllium oxide are inorganic materials, the storage conditions are not stringent and

286   they are not expected to degrade.

287

288   Room temperature storage is fine for these materials. A statistical Analysis of Variance (ANOVA) was

289   done and there was no difference in the data from day 1 from the data analyzed on day 30 (See Data in

290   Table A1-8). Table A1-9 shows that the dye solution (detector solution) is stable for at least 12 weeks

291   when stored on a laboratory bench.

292

293   **4.5 Interference with other elements**

294

295   Table A1-7 shows that this method is not sensitive to interference by other elements. This is due to

296   several reasons. First, EDTA in the detection solution binds many of the other elements; second, the high

297   pH of the measured solution, pH 12+, causes most other metals to precipitate; and third, the attachment

298   center in the dye is only able to fit a specific sized moiety, which is beryllium ion (see LANL paper in

299   Appendix 4 for a more thorough discussion). Note that if there is a very high concentration of another

300   element which results in coloration or haziness of the measurement solution due to suspended particles,

301   then one needs to either wait until the precipitate settles to the bottom of the cuvet or re-filter (syringe

302   filter) the solution so that the measurement solution is always colorless and clear. **Any color or haziness**

303   **in the measurement solution will interfere with fluorescence measurement.** Color and haziness may

304   be produced if the interferents are in very high concentration, as was the case in Table A1-7 for iron

305   (which formed a colored precipitate) or for titanium, where there were still some suspended titanium oxide

306   particles in the measurement solution.

307

APPENDIX 1

309 *Table A1-1:* Method detection limit data for 20x dilution

310 *Table A1-2:* Ocean Optics instrument detection limit data: HBQS test

311

312 *Table A1-3:* Recovery of beryllium from spiked Whatman 541 filters

313 *Table A1-4:* Analysis of spiked Whatman 541 filters by fluorescence and recovery confirmation of beryllium

314 using 1% ammonium bifluoride solution

315 *Table A1-5:* Analysis of spiked Whatman 541 filters by fluorescence

316 *Table A1-6:* Analysis of spiked MCE filters by fluorescence

317 *Table A1-7:* Interference Study – To look into interference caused by other elements

318 *Table A1-8:* Long term experiment to determine aging of samples

319 *Table A1-9:* Long term experiment to determine stability of detector (with HBQS dye) solution.

320 *Table A1-10:* Field data from a LANL machine shop- comparison with ICP

321 *Table A1-11:* Field data from a LANL firing range- comparison with ICP and recovery of beryllium from

322 Whatman 541 using 1%ammonium bifluoride.

323

324 In many of these tables the procedures that were followed are given in *NIOSH Technical Report,*

325 *Guidelines for air sampling, analytical method development and evaluation, 1995, Publication 95-117.*

326 Page numbers from these reports are listed in individual tables.

327   Table A1-1: *Method Detection Limit Data for 20x Dilution*

328   • Media used: 541 filter paper

329   • 20x dilution (Volumetric ratio of detection to dissolution solution 19:1)

330   •

331

sample	μg	irradiance
1	0.02	0.01
2	0.02	0.009
3	0.02	0.01
4	0.02	0.009
5	0.02	0.009
6	0.1	0.03
7	0.2	0.054
8	0.2	0.057
9	0.2	0.057
10	0.2	0.054
11	0.2	0.054

332   Detection limit was calculated to be 13.6ng/filter paper as given in Appendix 3, p-65,

333   NIOSH Technical Report. For this method we assumed a detection limit of 0.02μg and

334   then did 5 samples at this level, one at 5X level and 5 at 10X level.Calculation method

335   also given in Appendix 4 - See section on "detection limits"

336   Table A1-2: *Ocean Optics Instrument Detection Limits Data: HBQS test*

337

14

338   • 20x dilution (Volumetric ratio of detection to dissolution solution 19:1)

339

sample	µg	irradiance measurement
1	0.006	0.026
2	0.006	0.027
3	0.006	0.025
4	0.006	0.027
5	0.006	0.026
6	0.030	0.044
7	0.060	0.071
8	0.060	0.070
9	0.060	0.071
10	0.060	0.070
11	0.060	0.068

340

341   Detection limit was calculated to be 4.15ng/filter paper as given in Appendix 3, p-65,

342   NIOSH Technical Report. For this method we assumed a detection limit of 0.06µg (6ng)

343   and then did 5 samples at this level, one at 5X level and 5 at 10X level.

344   Calculation method also given in Appendix 4- See section on "detection limits"

345

346   Table A1-3: *Recovery of Beryllium from Spiked Whatman 541 Filters.*

347

Sample: Concentrations chosen around DOE Action limit of 0.2µg/filter

Date: 11/12/03

Instrument: Ocean Optics, 2-sec integration, 3 avg., measured at 475.42nm

Dilution: 20x dilution (Volumetric ratio of detection to dissolution solution 19:1)

348

Standard, ppb	0.0	0.2	1.0	2.0	4.0	10.0	Slope	Intercept
Intensity	0.012	0.026	0.081	0.155	0.283	0.710	0.069649	0.01151

349

350

Calibration curve fit			
Standard, ppb	Intensity	Calculated Conc, ppb	%Error
0	0.012	0.007	
0.2	0.026	0.208	-4.04
1	0.081	0.998	0.22
2	0.155	2.060	-3.01
4	0.283	3.898	2.55
10	0.710	10.029	-0.29

351

352   Results on Samples

Sample ID		Intensity	Be, µg/swipe
0.1µg Be	1	0.080	0.098
	2	0.081	0.100

	3	0.081	0.100
	4	0.081	0.100
	5	0.081	0.100
	6	0.081	0.100
	1	0.133	0.174
0.2µg Be	2	0.154	0.205
	3	0.152	0.202
	4	0.146	0.193
	5	0.152	0.202
	6	0.139	0.183
	1	0.298	0.411
0.4µg Be	2	0.278	0.383
	3	0.310	0.429
	4	0.307	0.424
	5	0.291	0.401
	6	0.291	0.401

353 · Table A1-4: *Analysis of spiked Whatman 541 filters by fluorescence and ICP and*

354 *recovery confirmation of beryllium using 1% ammonium bifluoride solution*

355 **Recovery results for two action levels of 0.2 and 3 ug/swipe. Six sets of samples at 0.1x, 0.5x**

356 **1.0x and 2x the action limit per the NIOSH Technical manual Section A page 10. Numbers**

357 **for 0.4 ug/swipe loading are in table A1-3. After dissolution, the filters were analyzed by**

358 **ICP and no appreciable beryllium was found.** Mark to send the method

359 The spiked Whatman 541 filter (wipe) was treated with 1%ammonium bifluoride by

360 mechanical agitation and the filtrate analyzed by fluorescence and ICP. To evaluate

361 residual beryllium on the wipe it was further treated with standard ICP protocols with

362 acids and analyzed.

363

DOE ACTION LEVEL 1: 0.2μg/wipe			DOE ACTION LEVEL 2: 3μg/wipe		
	[Be] μg			[Be] μg	
Spike Level Be, μg	Fluorescence	ICP Filtrate	Spike Level, Be, μg	Fluorescence	ICP Filtrate
0	0.000	0.002	0.3	0.297	0.309
0	0.000	0.002	0.3	0.297	0.311
0	0.000	0.002	0.3	0.310	0.312
0	0.000	0.002	0.3	0.310	0.306
0	0.000	0.001	0.3	0.310	0.316
0	0.000	0.001	0.3	0.300	0.312
0.02	0.019	0.022	1.5	1.364	1.400

0.02	0.021	0.023	1.5	1.578	1.578
0.02	0.019	0.023	1.5	1.690	1.674
0.02	0.021	0.023	1.5	1.696	1.623
0.02	0.019	0.023	1.5	1.616	1.582
0.02	0.019	0.024	1.5	1.578	1.538
0.1	0.093	0.106	3	3.031	2.965
0.1	0.089	0.107	3	3.034	2.948
0.1	0.099	0.106	3	3.050	3.014
0.1	0.090	0.107	3	3.222	3.071
0.1	0.098	0.105	3	3.066	2.930
0.1	0.096	0.107	3	2.734	2.623
0.2	0.189	0.207			
0.2	0.190	0.213			
0.2	0.184	0.219			
0.2	0.193	0.217			
0.2	0.196	0.219			
0.2	0.198	0.221			

364

365

366   Table A1-5: *Analysis of Spiked#541 Filters by Fluorescence*

367   Different lots of Whatman 541 filters have different amounts of residual acid. To ensure that this issue

368   does not interfere with the results, five different lots of filters were spiked and analyzed. The results show

369   that different filter lots still give similar results.

370

   Date: 10/29/2003

   20x dilution (Volumetric ratio of detection to dissolution solution 19:1)

   Fluorescence Intensity: 2-sec integration at 475.42nm, average of three readings

371

STANDARDS ppb							
Concentration (ppb)	0.0	0.2	1.0	2.0	4.0	Slope	Intercept
Intensity	0.012	0.027	0.082	0.153	0.274	0.065618	0.015109

372

Calibration curve fit			
ppb	Intensity	Calculated Concentration, ppb	%Error
0	0.012	-0.047	
0.2	0.027	0.181	9.40
1	0.082	1.019	-1.94
2	0.153	2.101	-5.07
4	0.274	3.945	1.37

373

374   Analysis of spiked filters. Each set of four filters was a different #541 lot.

Sample ID	Intensity	μg/filter
B1108930 Be 0	0.014	-0.002

20

B1108930 Be-1	0.150	0.206
B1108930 Be-2	0.148	0.203
B1108930 Be-3	0.155	0.213
814411 Be 0	0.013	-0.003
814411 Be-1	0.147	0.201
814411 Be-2	0.148	0.203
814411 Be-3	0.150	0.206
D1291860 Be 0	0.012	-0.005
D1291860 Be1	0.152	0.209
D1291860 Be2	0.151	0.207
D1291860 Be3	0.148	0.203
B1078249 Be 0	0.012	-0.005
B1078249 Be-1	0.157	0.216
B1078249 Be-2	0.149	0.204
B1078249 Be-3	0.148	0.203
D1330798 Be 0	0.012	-0.005
D1330798 Be1	0.147	0.201
D1330798 Be2	0.153	0.210
D1330798 Be3	0.151	0.207

375 Table A1-6: *Analysis of Spiked MCE Filters by Fluorescence*

Sample: Be (as solution) recovery from MCE air filters, in triplicate + sample with no filter

Date: 2/9/2004

20x dilution, 2-sec integration, 3 avg.

376

377 Calibration data at 475.42nm from Ocean Optics Instrument

	STANDARDS ppb							
Conc, ppb	0.0	0.2	1.0	2.0	10.0	20.0	Slope	Intercept
Intensity	0.011	0.02	0.063	0.11	0.51	1.024	0.050571	0.01

378

379 Calibration data fit

	Intensity	Calculated Concentration, ppb	%Error
Blanks	0.011	0.023	
0.2	0.020	0.201	-0.43
1	0.063	1.051	-5.12
2	0.110	1.981	0.97
10	0.510	9.890	1.10
20	1.024	20.054	-0.27

380

381

Sample ID	Intensity	Be, µg/wipe
0.02µg Be no filter	0.025	0.03
0.02µg Be-A	0.021	0.02
0.02µg Be-B	0.022	0.02
0.02µg Be-C	0.025	0.03

0.2µg Be no filter	0.112	0.20
0.2µg Be-A	0.115	0.21
0.2µg Be-B	0.106	0.19
0.2µg Be-C	0.118	0.21
2µg Be no filter	1.035	2.03
2µg Be-A	1.032	2.02
2µg Be-B	1.039	2.04
2µg Be-C	1.027	2.01

382 *When the results in this table are compared to that of the others (e.g., A1-6), it shows that the*

383 *results are as expected and that use of either Whatman 541 or MCE does not change the*

384 *conclusions. This is also seen in the Inter-laboratory study shown Appendix 5 and 6.*

385   Table A1-7: *Interference Study with Other Metals*

386   Intensities taken from the Ocean Optics Flourometer

387   20x dilution (Volumetric ratio of detection to dissolution solution 19:1)

388

389

	0 Be	100nM Be	% Difference	1uM Be	% Difference
Be	0.005	0.112	-	1.078	-
0.4mM Al	0.004	0.112	0.00	1.054	0.00
0.4mM U	0.004	0.11	1.79	1.06	-0.57
2mM Ca	0.004	0.112	0.00	1.057	-0.28
0.04mM Li	0.004	0.112	0.00	1.06	-0.57
0.4mMPb	0.004	0.111	0.89	1.105	-4.84
0.4mM Zn	0.003	0.112	0.00	1.103	-4.65
0.4mM Fe	0.003	0.101	9.82	0.925	12.24
0.4mM V	0.003	0.114	-1.79	1.083	-2.75
0.4mM Sn	0.003	0.113	-0.89	1.105	-4.84
0.4mM W	0.003	0.116	-3.57	1.103	-4.65
0.4mM Cu	0.003	0.114	-1.79	1.062	-0.76
0.4mM Ni	0.004	0.114	-1.79	1.074	-1.90
0.4mM Co	0.005	0.111	0.89	1.03	2.28

390   Fe has the highest interference and some precipitate was noticed at the bottom of the

391   cuvet. When these samples were looked at again after standing (for four hours), the

392   solution had cleared and as shown below no interference was seen.

	0 Be	100nM Be	% Difference	1uM Be	% Difference

Be	0.009	0.215		1.403	
0.4mM Fe	0.01	0.215	0.00	1.403	0.00

393

394

Interference data on Titanium*

395

Fluorometer used: Turner Quantech, 20x dilution

		Beryllium (µg) by fluorescence	
Amount of Be on filter, µg	Amount of TiO$_2$ on filter, mg		after additional filtration step
0.20	0.00	0.20	0.20
2.00	0.00	2.02	2.03
0.20	10.00	0.17	0.20
2.00	10.00	1.64	2.02
0.20	20.00	0.17	0.21
2.00	20.00	1.65	2.04

396 *Titanium was analyzed separately on the request of Beryllium Health and Safety Committee.*

397 *This was done as titania powders are often used in paint formulations, and thus it is frequently*

398 *present when swiping painted surfaces or in atmospheric sampling.*

399   Table A1-8: *Long Term Experiment to Determine Aging of Samples on Wipes*

400

401   Stability check as per NIOSH Technical manual, page 15

402

403   Sample on spiked 541 filter aged for various periods (storing conditions –Lab bench)

404

Whatman 541

0.1 µg Be/filter

20x dilution (Volumetric ratio of detection to dissolution solution 19:1)

405

Sample#	Intensity	Sample#	Intensity	Sample#	Intensity
1-day		7-days		14-days	
#1	0.095	#13	0.099	#22	0.095
#2	0.096	#14	0.093	#23	0.098
#3	0.099	#15	0.096	#24	0.099
#4	0.095	#16	0.098	21-days	
#5	0.097	#17	0.097	#25	0.095
#6	0.096	#18	0.096	#26	0.094
#7	0.098	10-days		#27	0.096
#8	0.094	#19	0.096	30-days	
#9	0.096	#20	0.097	#28	0.098
#10	0.096	#21	0.099	#29	0.099
#11	0.097			#30	0.094
#12	0.096				

406

408   Table A1-9: *Long Term Experiment to Determine Stability of Detection solution*

409

410   Instrument Used: Ocean Optics

411   Storage Condition: Stored in a dark colored bottle on a lab bench.

412

HBQS Reagent Stability
Be standard curve with 12-wk-old vs new
preparations of HBQS mix
2-sec integration time

413

| 414 | Table A1-10: *Field data from a LANL Machine Shop (sample numbers* |
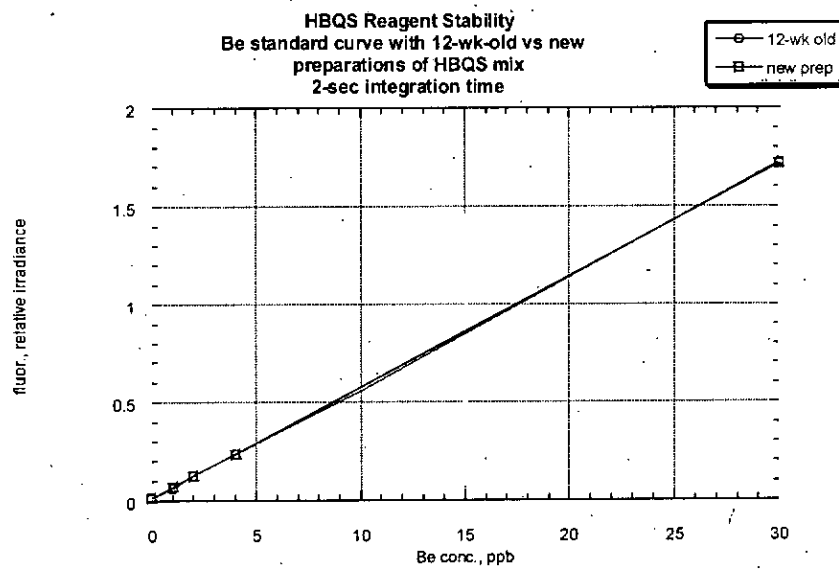
414   Table A1-10: *Field data from a LANL Machine Shop (sample numbers*

415   *200301922) or a Firing Point (sample numbers 200301845)-Comparison with ICP*

416

417   •   Side by side samples were collected at a firing point or a machine shop where beryllium contamination was

418   expected by using wipes (Whatman 541) on a surface area of 100 square cm.

419   •   Wipe 1 was analyzed by ICP-AES (modified OSHA 125G).

420   ▪   Wipe 2 was analyzed with the fluorometric method. An aliquot of the same dissolution solution was also

421   analyzed by ICP-AES.

422   ▪   Both type of samples are fom using beryllium metal, but an oxide skin is usually formed on the beryllium

423   particles, which is expected to be more for the samples from the firing range.

424   ▪   Although wipe 1 and wipe 2 (taken from adjacent areas) are expected to result in generally similar results in

425   terms of beryllium contamination, but at these low levels of contamination there is a finite probability that

426   there may be a large particle in one of these adjacent areas resulting in large variation of beryllium

427   concentration between the two.

428

Sample #		Wipe 1	Wipe 2		RPD	RPD
		ICP Result $\mu g/100\ cm^2$	Fluorometric Result $\mu g/100\ cm^2$	ICP of Fluorometric Dissolution Solution $\mu g/100\ cm^2$	Wipe 1 vs. Wipe 2	Wipe 2 ICP vs. Fluoro
200301845	A	0.04	0.03	0.03	28.6%	0.0%
200301845	B	< 0.03	0.02	< 0.02		
200301845	C	0.29	0.11	0.13	87.1%	13.1%
200301845	D	27.8	8.86	11.0	103.3%	21.6%
200301845	E	0.06	0.07	0.06	9.5%	9.5%

200301845	D	< 0.03	0.02	< 0.02		
200301845	G	< 0.03	0.01	< 0.02		
200301845	H	< 0.03	0.01	< 0.02		
200301845	I	< 0.03	0.01	< 0.02		
200301845	J	< 0.03	0.01	< 0.02		
200301845	K	< 0.03	0.00	< 0.02		
200301845	L	< 0.03	0.02	< 0.02		
200301845	M	< 0.03	0.02	< 0.02		
200301922	A	0.74	1.02	1.03	31.9%	0.9%
200301922	B	0.38	0.34	0.33	10.4%	5.2%
200301922	C	0.32	0.30	0.27	4.9%	11.0%
200301922	E	6.83	8.50	8.79	21.8%	3.3%
200301922	D	7.94	7.75	7.71	2.4%	0.5%
200301922	G	5.69	7.35	7.86	25.4%	6.7%
200301922	H	12.7	15.1	15.3	17.8%	1.0%
200301922	I	14.4	14.3	14.7	0.6%	2.7%
200301922	J	12.8	13.6	12.7	6.7%	7.2%
200301922	K	10.8	11.0	10.8	1.6%	1.6%
200301922	L	21.5	19.0	17.5	12.6%	8.0%
200301922	N	6.98	9.08	9.00	26.1%	0.9%
200301922	O	18.8	25.3	25.2	29.4%	0.4%
200301922	P	6.79	11.7	10.9	52.7%	7.0%
200301922	Q	15.6	8.82	8.79	55.4%	0.4%
200301922	R	10.3	8.70	10.0	17.1%	13.9%
200301922	S	15.0	13.3	14.0	11.9%	5.1%
200301922	T	14.0	11.0	11.2	24.4%	1.9%

				Average of RPDs =	26.4%	5.5%
Average of Samples =	9.5	8.9	9.0		7.2%	1.0%

429

430

431 Table A1-11: *Field data from a LANL Firing Range (samples RW) and the*

432 *machine shop (samples GW)-Comparison with ICP and Dissolution Recovery*

433 *using Ammonium Bifluoride Solution This data is similar to the one in Table A1-10*

434 *where the sampling and analysis was carried out by another group at a different*

435 *time)*

436

437 20x dilution (Volumetric ratio of detection to dissolution solution 19:1)

438 Date: 10/3/2003

439

440 Samples using Whatman 541 filters as wipes were analyzed with the fluorometric method using 1%ammonium

441 bifluoride dissolution. An aliquot of the same dissolution solution (filtrate) was also analyzed by ICP-AES. Further, the

442 residue on the dissoluted filter was analyzed by following a standard ICP acid digestion to evaluate how much of

443 beryllium remained after the filters were dissoluted using ammonium bifluoride solution. The results showed that

444 dissolution procedure using 1% ammonium bifluoride was effective.

445

446

SAMPLE	fluor. test µg Be/filter	ICP Filtrate µg Be/filter	SAMPLE	fluor. test µg Be/filter	ICP Filtrate µg Be/filter
GW 2003-01923			RW 2003-01845		

32

A	0.347	0.350		A	0.030	0.030
B	0.137	0.130		B	0.017	<0.02
C	0.134	0.120		C	0.114	0.130
D	0.002	0.020		D	8.858	11.000
E	5.950	6.150		E	0.066	0.060
F	5.425	5.400		F	0.023	<0.02
G	5.143	5.500		G	0.011	<0.02
H	3.179	3.210		H	0.009	<0.02
I	6.423	6.600		I	0.010	<0.02
J	2.182	2.030		J	0.012	<0.02
K	4.236	4.170		K	0.002	<0.02
L	1.137	1.050		L	0.017	<0.02
M	0.007	0.020		M	0.016	<0.02
N	3.813	3.780				
O	5.313	5.290				
P	1.631	1.520				
Q	6.173	6.150				
R	10.440	12.000				
S	6.987	7.350				
T	7.027	7.160				

447

448 ICP performed by Chris Brink

449   # Appendix 2

450

451   **Table A2-1: Experiments to Evaluate effectiveness of Ammonium Bifluoride as**

452   **Recovery Solvent**

453   Using the LANL fluorescence method, good recoveries were obtained from both soluble and insoluble Be

454   compounds; see the table below:

455   *Table: Summary of results from Be extraction in 5 or 10 mL of 1% ammonium bifluoride & analysis by fluorometry;*

456   *mechanical agitation or sonication for 1 hour. (Masses treated were 10-20 mg for $BeSO_4 4H_2O$ and 5-10 mg for*

457   *BeO.)*

Sample	agitation method	% recovery ± std. dev. (n = 3)
458 Be sulfate	mechanical	99.8 ± 4.4
459 Be sulfate	sonication	106.6 ± 12.0
460 BeO	mechanical	90 ± 3
461 BeO	sonication	83 ± 3
462 Be sulfate / MCE filters	mechanical	98.6 ± 1.6
463 Be sulfate / MCE filters	sonication	110.4 ± 4.7
465 BeO / MCE filters	mechanical	94 ± 6
466 BeO / MCE filters	sonication	93 ± 6
467 Be sulfate / Whatman 504 filters	mechanical	98.1 ± 3.3
468 Be sulfate / Whatman 504 filters	sonication	101.3 ± 2.5

34

469	BeO / Whatman 504 filters	mechanical	86 ± 8
470	BeO / Whatman 504 filters	sonication	96 ± 5
471	Be sulfate / Ghost wipes	sonication	79.3 ± 2.4
472	BeO / Ghost wipes	sonication	40 ± 4
473	Be sulfate / Palintest wipes	sonication	87.6 ± 2.5
474	BeO / Palintest wipes	sonication	84 ± 2
475			

476 The results from the work summarized in the table show promise for the potential use of this extraction method for

477 on-site analysis. These experiments also indicate that Ghost wipes, used widely for surface sampling by industrial

478 hygienists, may not be appropriate for field-based monitoring of beryllium. Recovery results above 75% are

479 acceptable[7].

480 Beryllium oxide and Beryllium sulfate samples were obtained from Sigma Aldrich.

7 Kennedy ER, Fischbach TJ, Song R, Eller PM, Shulman SA [1995]: *Guidelines for Air Sampling and Analytical Method Development and Evaluation.* CDC/NIOSH: Cincinnati, OH; DHHS (NIOSH) Publication No. 95-117.

Appendix 3

482   Table A3-1: *Analysis of spiked Filters using suspension of Beryllium oxide*

483   *(UOX125 from Brush Wellman)*

484   Table A3-1: *Analysis of spiked Filters using suspension of Beryllium oxide*

485   *(UOX125 from Brush Wellman)*

486   • Comparison of mechanical agitation and heating (without agitation) on dissolution process using

487   1% ammonium bifluoride Whatman 541 filters spiked from a suspension

488   • Instrument used: Turner Quantech

489   • Expected numbers show a range as it was difficult to control the uniformity of the suspension.

490   **Calibration data**

ppb pre-dilute	ppb pre-dilute	std. Final ppb	Readback, final, ppb
0	0.36	0	0.02
10	10.16	0.5	0.51
40	39.56	2	1.98
200	196.35	10	9.82
800	791.68	40	39.58

Summary of results in µg Be/filter

BeO, µl	expected	rotated	75 °C	90 °C
3	0.2	0.19	0.23	0.21
15	1 to 1.2	0.65	1.11	1.20
60	4 to 5	2.68	4.54	4.20

491

492

493   **Data Details (see summary above)**

494

Rotated for 30 minutes		
Sample	Expected, µg/filter	µg/filter
Blank	0	0.00
3 A	0.2	0.21
3 B	0.2	0.21
3 C	0.2	0.15
15 A	1 to 1.2	0.85
15 B	1 to 1.2	0.60

37

15 C	1 to 1.2	0.49

60 B	4 to 5	2.87
60 C	4 to 5	2.48

495

496

	75C for 30 minutes			90C for 30 minutes	
sample	Expected, µg/filter	µg/filter	sample	Expected, µg/filter	µg/filter
Blank	0	0.00	Blank	0	0.00
3 A	0.2	0.28	3 A	0.2	0.18
3 B	0.2	0.19	3 B	0.2	0.23
3 C	0.2	0.22	3 C	0.2	0.22
			15 A	1 to 1.2	1.42
15 B	1 to 1.2	1.16	15 B	1 to 1.2	1.15
15 C	1 to 1.2	1.06	15 C	1 to 1.2	1.02
60 A	4 to 5	4.39	60 A	4 to 5	4.42
60 B	4 to 5	4.99	60 B	4 to 5	3.79
60 C	4 to 5	4.25	60 C	4 to 5	4.38

497

38

Table A3-2: *Analysis of Spiked Filters using Freshly Prepared Suspension of*

Beryllium Oxide (UOX125 from Brush Wellman)

500

501 Instrument used: Turner Quantech,

502 Dissolution: Sample Heated to 80C (using a heating block) without stirring in 1% ammonium bifluoride

503 After dissolution, the solution was analyzed using both by fluorescence and ICP. (NA=Not analyzed).

504 Some of the samples were analyzed using accepted acid digestion and ICP protocol to ensure that the

505 filters had the anticipated amount of beryllium oxide

Spike Level		μg/filter (Whatman 541)		
Be μg	sample	fluor	ICP of filtrate	ICP digestion
0	A	0.00	0.00	
0	B	0.00	NA	
0.1	A	0.08	0.08	
0.1	B	0.06	0.06	
0.1	C	0.08	0.08	
0.1	D	0.11	NA	
0.1	E	0.09	NA	
0.1	F			0.13
	Average	0.08	0.07	
	Std Dev	0.018	0.012	
0.2	A	0.18	0.18	
0.2	B	0.19	0.19	
0.2	C	0.20	0.20	
0.2	D	0.15	NA	
0.2	E			0.20
0.2	F	NA	NA	0.26
	Average	0.18	0.19	
	Std Dev	0.022	0.010	
0.3	A	0.28	0.28	
0.3	B	0.26	0.26	
0.3	C	0.29	0.28	
0.3	D	0.27	NA	
0.3	E	0.23	NA	
0.3	F			0.29
	Average	0.27	0.27	
	Std Dev	0.023	0.012	

Spike Level		μg/filter (Whatman 541)		
Be μg	sample	fluor	ICP of filtrate	ICP digestion
0.0	C	0.00	0.00	
0.0	D	0.00	NA	
0.0	E	0.00	NA	
0.0	F	0.00	NA	
0.0	G	0.00	NA	
0.02	A	0.01	0.01	
0.02	B	0.02	0.02	
0.02	C	0.02	0.02	
0.02	D	0.01	NA	
0.02	E	0.01	NA	
	Average	0.014	0.02	
	Std Dev	0.0055	0.006	
1.5	A	1.17	1.20	
1.5	B	1.11	1.10	
1.5	C	1.35	1.33	
1.5	D	1.78	NA	
1.5	E	1.52	NA	
1.5	F			1.47
	Average	1.39	1.21	
	Std Dev	0.2726	0.115	
3.0	A	3.40	3.42	
3.0	B	3.82	4.06	
3.0	C	3.06	3.02	
3.0	D	3.09	NA	
3.0	E	3.13	NA	
3.0	F			2.70
	Average	3.30	3.50	
	Std Dev	0.3205	0.525	

506 **Appendix 4**

507

508 Publication: *Development of a New Standard Method for the Detection of Beryllium on*

509 *Surfaces*

Development of a New Standard Method for the

Detection of Beryllium on Surfaces

514   *Edel M. Minogue, Deborah S. Ehler, Anthony K. Burrell**, T. Mark McCleskey*, Tammy P.*

515   *Taylor*

516   ⌐   Chemistry Division (C-SIC), Los Alamos National Laboratory, MS J514, Los Alamos,

517   New Mexico 87545, USA.

518   ABSTRACT

519   A rapid, quantitative, sensitive test for the detection of beryllium on surfaces has been developed.

520   The method is based on the fluorescence of beryllium bound to sulfonated hydroxybenzoquinoline at

521   pH 12.8, which emits at 475 nm when excited at 380 nm, and includes a novel dissolution technique.

522   The intensity of fluorescence is linear with respect to beryllium concentration. A detection limit of

---

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     (T.M.M.) tmark@lanl.gov

523   0.02 μg Be/ 100 cm^2 has been achieved, which is ten times lower than the DOE recommended

524   working limit for non-beryllium work areas(8). Interference studies have been carried out with a

525   variety of metals including Al, Fe, Pb, U, Cd, Cr, Hg, Ca, W, Ni, Co and Cu with minimal or no

526   interferences found for detection of Be at 100 nM in the presence 0.4 mM of the other metal. The

527   method has been proven successful under various operating conditions including the detection of

528   beryllium on a variety of surfaces both in laboratory settings and in field trials. It fulfills the

529   requirements for a fast, inexpensive, field deployable method of detection of beryllium on surfaces.

530   KEYWORDS: Beryllium, fluorimetric detection, HBQS, environmental monitoring

531   INTRODUCTION

532   The unique properties of beryllium (Be) have lead to many applications ranging from the

533   aerospace and nuclear industry to manufacturing and electronics. Unfortunately, beryllium is a Class

534   A EPA carcinogen and when inhaled into the lungs can cause the incurable and potentially fatal lung

535   disease, chronic beryllium disease (CBD). Therefore, the monitoring of beryllium in occupational

536   environments is of vital importance. Congress has recently passed limits of Be exposure of 2 μg / m^3

537   (9), and DOE facilities have adopted even more stringent levels that include 0.2 μg / m^3 for airborne

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8 CFR (Code of Federal Regulations), Title 10, Energy, Part 850, Department of Energy, **2001**

parts 500 to end.

9 A Comparison and Critique of Historical and Current Exposure Assessment Methods for

Beryllium: Implications for Evaluating Risk of Chronic Beryllium Disease; Kolanz, M.E. *Appl.*

Occupational and Environ. Hygiene **2001a**, 16 5 559-567.

538 levels and 0.2 μg / 100 cm^2 as a surface level for the release of items from beryllium areas[8]. For

539 release to another DOE facility working with beryllium, contamination levels are not to exceed 3.0

540 μg / 100 cm^2 [8].

541 To date, the standard method for the detection of beryllium on surfaces is a surface swipe

542 technique described by OSHA (ID-125G) (10). The method involves swiping a 10 cm x 10 cm area

543 with a cellulose ester membrane and subsequently digesting the membrane with hydrogen peroxide

544 and sulfuric acid. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is used to

545 quantify beryllium in the samples. Although straightforward, the procedure can be costly, turnaround

546 time is slow, and it is unsuitable for field use. In addition, the current OSHA method requires

547 consumption of the entire sample in order to meet detection levels. Consequently, verification of

548 results can be difficult if concerns arise post-analysis. There have been attempts to develop a swipe

549 analysis technique based on absorbance changes (11·12) but they have been unable to obtain the

550 necessary quantitative detection limits of 0.02 μg / 100 cm^2 for NIOSH approval.

10 Metal and Metalloid Particulates in Workplace Atmospheres (ICP Analysis), Method No. ID-125G, Control No. T-ID-125G-FV-03-0209-M,

http://www.osha.gov/dts/sltc/methods/inorganic/id125g/id125g.html#table1

11 Beryllium Colorimetric Detection for High Speed Monitoring of Laboratory Environments; Taylor, T.P.; Sauer, N.N. *J. Hazard. Mater.* B93 **2002** 271-283.

12 Beryllium in the Environment: A Review; Taylor, T.P.; Ding, M.; Ehler, D.S.; Foreman, T.M.; Kaszuba, J.P.; Sauer, N.N. *J. Environ. Sci. Health* A38 **2003** 2 439-469.

551 Fluorescence is an ideal method of detection because it is extremely sensitive, non-destructive and

552 can be performed quickly. Fluorescent detection of Be has been reported since the 1950s with

553 literature reports on a variety of fluorescent indicators including morin (13,14,15), chromotropic acid

554 (16), and Schiff bases (17). Despite the many reports of fluorescent indicators for Be, a complete

555 system for the fluorescence detection of Be has yet to be approved by NIOSH, and there is no

556 commercial fluorescent Be detector kit. A complete, robust fluorescent detection method requires

557 three key features: a dissolution method that is able to dissolve Be and BeO and remains compatible

558 with the fluorescence indicator; tolerance to a wide variety of interferences; a minimal number of

559 simple steps from dissolution to detection. Typical dissolution methods for the dissolution of BeO

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13 Fluorometric Determination of Traces of Beryllium; Laitinen, H.A.; Kivalo P.; *Anal. Chem.* **1952** 24 9 *1* 467-1471.

14 Determination of Beryllium in Water by Ion Exchange Spectrofluorimetry; Capitan, F.; Manzano, E.; Navalon, A.; Vilchez, J.L.; Capitan-Vallvey, L.F. *Analyst* **1989** 114 *8* 969-973.

15 Optical Sensor for Beryllium Based on Immobilized Morin Fluorescence; Saari, L.A.; Seitz, W.R. *Analyst* **1984** 109 *5* 655-657.

16 Chromotropic Acid as a Fluorogenic Reagent. 1. Fluorometric-Determination of Beryllium; Pal, B.K.; Baksi, K. *Microchim Acta* **1992** *108* 275-283.

17 Metal-Complexes of Aromatic Schiff-Base Compound. 2. Fluorescence of Beryllium and Scandium Complexes and Their Use in Fluorimetry; Morisige, K. *Anal. Chim. Acta* **1974** 73 *2* 245-254.

560　from a swipe involve concentrated inorganic acid and heating; in addition some methods use

561　hydrogen peroxide. Such conditions are not compatible with any known fluorescent indicator, so the

562　solution must be evaporated to dryness and further treated before it can be added to the fluorescent

563　indicator. The work presented herein is a description of the development of a rapid fluorescence

564　method for the quantitative detection of beryllium on surfaces using the indicator 10-

565　hydroxybenzo[h]quinoline-7-sulfonate (10-HBQS). The method is beryllium specific, inexpensive,

566　applicable to different swipe materials, and field deployable. Detection limits of 0.02 μg beryllium /

567　$100 \ cm^2$ swiped surface (one tenth of the DOE required action level of 0.2 μg / $100 \ cm^2$) have been

568　achieved. We are currently working with the National Institute for Occupational Safety and Health

569　(NIOSH) for approval of this method for beryllium detection.

570　　In order to eliminate the time-consuming and non-fieldable digestion steps of current standard

571　methods, the use of a fluoride-based medium to dissolve Be was investigated. It was found that Be

572　metal was dissolved within seconds in 1% ammonium bifluoride $(NH_4)HF_2$. However, high-fired

573　BeO is the most difficult form of Be to dissolve. We tested the dissolution of 10 mg quantities of

574　BeO with 50 mL of 1% $(NH_4)HF_2$ to demonstrate that 80% of the oxide form could be dissolved in

575　just 15 minutes with minimal agitation. Fluoride, usually in the form of HF, is well noted for its

576　ability to penetrate and dissolve metal oxides (18). Most fluorescent indicators reported do not

577　tolerate the presence of fluoride. The few reports of indicators that tolerate fluoride have

578　complicated procedures involving heating with acid for dissolution and a titration process to obtain

18 Cotton, F.A.; Wilkinson, G.; Advanced Inorganic Chemistry 5[th]ed. Wiley-Intersciemce: New

York, 1988.

579   the final pH. The duration and complexity of those procedures do not lend themselves easily to field

580   analysis.

581   Having screened several potential ligands, 10-HBQS, a water-soluble fluorescent dye, was

582   selected for the development of the fluorescence method. In an previous study, The selection of 10-

583   HBQS stemmed from work done in a previous study by Matsumiya et al (19) where they studied

584   beryllium in urban air and showed that 10-HBQS, hydroxybenzoquinoline (HBQ) chelated the

585   Be(II) ion. In another work, they used the precursor HBQ as a pre-column chelating reagent for the

586   determination of beryllium in water by reversed-phased high-performance liquid chromatography

587   (20). HBQ fluorescent detection involves the formation of a six-membered chelate ring with Be. A

588   tightly bound hydrogen bonded proton leads to weak triplet emission at 580 nm. When the proton is

589   displaced by a metal such as beryllium, fluorescence emission is observed at 475 nm. However,

590   because HBQ is sparingly soluble in water, we selected the sulfonated derivative 10-HBQS for our

591   studies. Although HBQ was previously commercially available, neither HBQ nor 10-HBQS are

19 A Novel Fluorescence Reagent 10-hydroxybenzo[h]quinoine-7-sulfonate, for Selective Determination of Beryllium(II) Ion at pg cm^{-3} Levels; Matsumiya, H.: Hoshino, H.; Yotsuyanagi, T. *Analyst* **2001**, 126, 2082-2086.

20 Selective Determination of Beryllium (II) Ion at Picomole per Decimeter Cubed Levels by Kinetic Differentiation Mode Reversed-Phase High-Performance Liquid Chromatography with Fluorometric Detection Using 2-(2'-Hydroxyphenyl)-10-hydroxybenxo[h]quinoline as Precolumn Chelating Reagent; Matsumiya, H.; Hoshino, H.; *Anal. Chem.* **2003** 75 413-419.

592   currently commercially available nor are there useful synthetic procedures published. Therefore, we

593   developed synthetic pathways for both of these compounds (21).

594

595   EXPERIMENTAL

596   *Apparatus:* A miniature fluorescence spectrometer from Ocean Optics (S2000-FL) was

597   customized to incorporate a UV LED with an excitation wavelength of 380 nm (continuous mode).

598   Instrument calibration was carried out using a LS-1-CAL white light source. Detection was carried

599   out using the USB2000 Miniature Fiber Optic Spectrometer connected to the serial port of a laptop

600   computer. Spectra were obtained in the relative irradiance mode using Ocean Optics OOIBase32

601   Software. The wavelength of emission is 475 nm. The detection limit of the set-up was 0.06 ppb Be.

602   Results were verified by ICP-AES, Jobin Yvon Inc., Edison, New Jersey. This particular instrument

603   has a detection limit of approximately 100 ppt Be, allowing good comparison with the low levels of

604   detection obtainable with our fluorimetric method. Verification of side-by-side swipes were carried

605   out by the standard method for detection of beryllium on surfaces (i.e. digestion of swipe and then

606   ICP-AES). The pH was measured using an Orion pH / ISE Model 710 meter which was calibrated

607   using pH 4, 7 and 10 buffer solutions (Fisher Scientific Inc.).

608

609   *Reagents and Solutions:* Solid forms of beryllium used included beryllium oxide (BeO 99%,

610   Acros) and beryllium sulfate ($BeSO_4$, Acros). All solid forms of beryllium were handled in a

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21   The Generation and Trapping of 7,8-quinolyne: A New Synthesis of 10-hydroxybenzo[*h*]quinoline and Access to 7-substituted Derivatives; Collis, G.E., Burrell, A.K.; *Tetrahedron Lett*; submitted.

611   HEPA-filtered glove box by a beryllium-trained worker. The following stock solutions were

612   prepared: $(NH_4)HF_2$ (Aldrich), 1 % wt / vol in water, 1.1 mM HBQS pH adjusted to pH 12 with 10

613   M NaOH (Fisher), 100 mM L-Lysine monohydrochloride (Aldrich) at pH 11-12, and 1 mM EDTA

614   disodium dihydrate (J.T. Baker, Inc.). ICP standard solutions (1000 µg / mL metal; SPEX

615   Centriprep) of the following metals were used in interference studies: Al, U, Ca, Li, Pb, Zn, Fe, V,

616   Sn, W, Cu, Ni, Co, Cd, Cr and Hg. Deionized water (MilliQ®) was used throughout.

617   Whatman® 541 filters (47 mm diameter) are used as the standard swipe in our experiment. These

618   cellulosic filters are currently utilized by Los Alamos National Laboratory industrial hygienists for

619   the NIOSH approved method of Be testing and from this point will be referred to as *swipes*. The

620   term *filter* will be used when a surface has not been swiped (e.g. for experiments where filters are

621   spiked with known concentrations of Be).

622

623   METHOD

624   *General Procedure:* The detection reagent was prepared by the addition of 12.5 mL of 10.7 mM

625   EDTA and 25 mL of 107 mM L-lysine monohydrochloride to 3 mL of 1.1 mM 10-HBQS. The pH

626   was adjusted to 12.85 with the careful addition of 10 M NaOH and water added to a total of 50 mL.

627   Beryllium standards were generated using Be spectrometric standard solutions diluted into 1%

628    $(NH_4)HF_2$ for the desired concentrations. For calibration curves a 0.1-mL aliquot of each standard

629   solution was added to 1.9 mL of the detection reagent, and spectra were taken at a set integration

630   time. A linear increase in intensity at 475 nm with respect to increasing beryllium concentration was

631   observed (Fig. 1). This enabled the conversion of intensities to concentrations. The amount of Be

632   (µg / 100 cm^2) in the area swiped (A) was then obtained by equation 1, whereby C_s (µg / L) is the

633 concentration for a given sample with a volume of V_s (L), and C_b (μg / L) is the concentration of the

634 blank with a volume of V_b (L). F_d is the dilution factor in this method:

635

636 $$[Be]\left(\mu g / 100 cm^2\right) = \frac{F_d \times \left[C_s V_s - C_b V_b\right]}{A}$$

637

638 A result of 2 ppb in our method corresponds to 0.2 μg Be on the swipe. Results must be

639 normalized if an area greater than 100 cm^2 is swiped. If the concentration of beryllium is out of

640 range (too high), then the instrument is recalibrated using higher standards and a shorter integration

641 time. In this way, the range of analysis can be extended. For quality control purposes, a calibration

642 standard and a reagent blank are analyzed at least once every 20 samples.

643

644 *Dissolution study*: The dissolution study was comprised of two areas of interest: the suitability of

645 the Be-dissolving agent and the time-minimization of this step. Preliminary studies of dissolution

646 show 1% $(NH_4)HF_2$ dissolves Be and BeO at levels within the required detection range (i.e. 0.02 μg

647 – 3.0 μg Be / swipe). Moreover, $(NH_4)HF_2$ does not interfere with 10-HBQS, the ligand of choice.

648 Time analyses were carried out in order to minimize the dissolution time while ensuring that

649 beryllium was dissolved. A 0.15 μg BeO / mL suspension was made by adding 7.5 μg of BeO to 50

650 mL H_2O. A filter was spiked with a 5-μL aliquot of the suspension. The spiked filter was placed in a

651 tube, and 5 mL of 1% $(NH_4)HF_2$ was added, the tube capped and then rotated. A 0.5-mL aliquot was

652 taken at set intervals and added to 1.5 mL of the dye reagent mix in a cuvette. Spectra were taken for

653 each interval, and the intensity at 475 nm observed.

654

655 *Interference Study*: The following metal solutions were made by dissolving the standard ICP

656 metal solution with 1% $(NH_4)HF_2$ such that the end concentration of the 0.1 mL aliquot in the 1.9

657 mL dye mix was between 0.04 mM and 2.0 mM: 0.4 mM Al, 0.4 mM U, 2.0 mM Ca, 0.4 mM Li, 0.4

658 mM Pb, 0.4 mM Zn, 0.4 mM Fe, 0.4 mM V, 0.4 mM Sn, 0.4 mM W, 0.4 mM Cu, 0.4 mM Ni, 0.4

659 mM Co, 0.04 mM Cd, 0.04 mM Cr, 0.04 mM Hg. Each sample was prepared in triplicate with (100

660 nM and 1 µM Be) and without Be. The interference metals were in ≥50,000 fold molar excess to the

661 Be present. Spectra were taken for each sample, and the intensity at 475 nm observed.

662

663 *Stability Study*: Both the stability of the detection reagent solution and the Be-$(NH_4)HF_2$

664 detection reagent solution were studied over time. A 100-mL solution of the detection reagent

665 containing 10-HBQS, EDTA and buffer was made as previously described. 1.9-ml aliquots? were

666 removed at set time intervals, 0.1 ml of Be standards in $(NH_4)HF_2$ were added and analyzed

667 fluorimetrically. The stability of the final samples was tested by keeping the first set of standards,

668 sealed in cuvettes, which were subsequently fluorimetrically analyzed on a weekly basis.

669

670 *Detection Limit:* The current required NIOSH detection limit is 0.2 µg Be/ 100cm^2. In order to

671 quantify the method detection limit, the following standards were prepared: five low-level standards

672 (0.02 µg - ten times lower than the required detection limit), five standards at the detection limit of

673 0.2 µg, one standard of 0.1 µg and a reagent blank. Filters were spiked with the standards and dried

674 for 20 minutes after which time 5 mL of $(NH_4)HF_2$ was added, followed by fluorimetric analysis.

675

676 *Procedure for the Swipe Test:* A 100-cm^2 surface was swiped with a Whatman$^®$ 541 filter

677 moistened with deionized water, in accordance with the procedure described in OSHA ID-125G[10]

678 and in ASTM D6966 (22). The swipe was then placed into a 15-mL polypropylene tube, and 5 mL

679 of the 1% -$(NH_4)HF_2$ solution was added. The tube was capped and then rotated (Barnstead /

680 Labquake tube rotator) for 30 min during which time the Be was dissolved. The solution was filtered

681 through a luer-locked PTFE (Millipore) or nylon 0.45 µm syringe filter. In a disposable, clear-sided

682 cuvette, 0.1 mL of the filtrate was added to 1.9 mL of the dye solution mix (20x dilution). The

683 cuvette was capped and briefly shaken, and a fluorescence spectrum taken ($\lambda_{excitation}$ = 380 nm;

684 $\lambda_{emission}$ = 475 nm). A set of Be standards using the same dye mix was also prepared and the

685 fluorescence spectra taken for each set of samples. A calibration curve of the intensities of Be at 475

686 nm versus beryllium concentration was plotted. From this the beryllium concentration in the sample

687 was obtained. The remaining Be filtrate was analyzed using ICP-AES, providing corroborative

688 results.

689

690 *Field Trials*: The implementation of our fluorimetric method on swipes from different

691 environments was investigated. Potentially Be-contaminated surfaces were swiped according to

692 OSHA and NIOSH procedures[10] by an industrial hygienist at Los Alamos National Laboratory in the

693 laboratory, in the beryllium workshop areas, and also in the field. A 100-cm^2 area was swiped and

694 the swipe placed in a tube. A 5-mL aliquot of $(NH_4)HF_2$ was added to the tube, which was

---

22 ASTM D6966 (2003) Standard Practice for Collection of Surface Wipe Samples for

Subsequent Determination of Metals. American Society for Testing and Materials (ASTM); West

Conshohocken, PA.

695 subsequently rotated for 30 min. The Be-$(NH_4)HF_2$ solution was decanted into a luer-locked syringe

696 filter and filtered. A 0.1-mL aliquot of the filtrate was added to 1.9 mL of the detection reagent and

697 the sample was fluorimetrically tested for Be. The remaining filtrate was sent for ICP-AES for

698 confirmational results.

699 In addition to this, 100 µL of potential interferents such as ethylene glycol, oil, and cleaning

700 agents were added to Be-spiked filters. The filters were then subject to fluorimetric analysis. This

701 was carried out in duplicate.

702 Side-by-side swipes from both a Be contaminated shop and firing points including surfaces such

703 as steel, aluminum and paint were also collected, with one swipe analyzed by the fluorimetric

704 method and the other by the digestion / ICP-AES method. The remainder of the Be-$(NH_4)HF_2$ filtrate

705 was also analyzed by ICP-AES.

706

707 RESULTS AND DISCUSSION

708 *Fluoride interference with indicator*: Based on preliminary experiments involving the dissolution

709 of BeO with $(NH_4)HF_2$, we needed a fluorescent indicator that could tolerate large concentrations of

710 fluoride. HBQS had previously been reported to tolerate up to 20,000,000 equivalents of fluoride[19].

711 Most other Be fluorescent indicators are readily susceptible to fluoride interference at only 300

712 equivalents. We tested the response of HBQS in the presence of 0.25% fluoride and found that it

713 responded well. The increase of intensity at 475 nm with respect to beryllium concentration as

714 exhibited in Fig. 1 is not only a indication of the effectiveness of the ligand 10-HBQS but also a

715 proof of the effectiveness of the ligand in the matrix containing $(NH_4)HF_2$.

716

717   *Dissolution study*: The dissolution of Be from the swipe into the $(NH_4)HF_2$ solution is the time-

718   limiting step for this otherwise instantaneous method. We minimized this by investigating the time

719   dependence for the dissolution of high fired BeO, one of the most inert forms of Be, spiked onto a

720   Whatman® 541 filter. The intensity of the sample at 475 nm increased with increasing dissolution

721   time up until 25 min. A direct overlap of the intensities at 25 min and 30 min was observed. No

722   further increase of the fluorescence was observed. Therefore 30 min was chosen as the dissolution

723   time for our experiments, providing a quick response time and near-complete dissolution.

724

725   *Interference Study:* Interference studies with a range of other metals have shown that even in

726   50,000-fold molar excess over Be, metals such as Pb, U, Hg or Cr show little (<1%) or no

727   interference (Table 1). The exception was that high concentrations of Fe (i.e. > 20 µM Fe) have a

728   negative effect on Be intensity of approximately 10% because suspended Fe precipitate absorbs light

729   at 380 nm. If, however, the Fe precipitate is allowed to settle for 4 hours or is filtered using a PTFE

730   or nylon filter, and is then reanalyzed, there is no interference. Having the Fe precipitate is an

731   advantage of working at a high pH. Therefore, it is recommended that, with fluorimetric analysis of

732   beryllium, if high iron content is suspected (e.g. due to swiping a rusty surface) or is evident from

733   the gold-orange color that appears when the HBQS mix is added, filter the solution or allow the

734   solution to settle until clear and colorless, and then carry out the fluorimetric analysis.

735

736   *Stability Study*: For the development of a field deployable method, it is essential that the reagents

737   are stable over a given period of time. Therefore, the stability of the dye mix solution (stored in

738   brown Nalgene HDPE bottles) was studied over time by running Be calibration curves made with

739   the aging dye. After 120 days, no decrease in response was observed. Beryllium standard solutions,

740   which contained the dye mix solution, were also studied over time. They remained stable over 28

741   days, thus enabling rapid on-site detection of beryllium with pre-prepared reagents and standards. It

742   should be noted that if the beryllium standards including the dye mix are to be stored for longer than

743   a week, the solutions should be stored in a screw-topped, sealable container.

744

745   *Detection Limit:* The method limit of detection (LOD) and the instrument detection limit were

746   determined according to NIOSH procedures (23). The low-level calibration standards were analyzed

747   and the average result obtained for replicate aliquots. The results obtained were graphed against the

748   mass of Be, and the linear regression equation $Y = mX + c$ enabled the evaluation of responses, Y^*_i,

749   for Be mass. The standard error of regression was calculated using equation 2 where N is the number

750   of data points:

751   $$s_y = \frac{\Sigma\left(Y^*_i - Y_i\right)^2}{(N-2)}^{-\frac{1}{2}}$$ (2)

752   A limit of detection of 13.6 ng / swipe (0.136 ppb) was achieved from equation 3 below:

753

23 Guidelines for Air Sampling and Analytical Method Development and Evaluation; Kennedy,

E.R., Fischbach, T.J., Song, R., Eller, P. M., Shulman, S. A.: **1995** DHHS (NIOSH) Publication No.

95-117.

754 $$LOD = \left(\frac{3s_y}{m} \right)$$ (2)

755   (*Field trial of swipe test:* The Be-$(NH_4)HF_2$ solutions from field swipes were analyzed by

756 both the fluorimetric method and ICP-AES. The recovery rate was 99.5 %, reinforcing the suitability

757 of the method to realistic environments (Table 3). Beryllium levels ranged from below the

758 fluorimetric detection limit <0.02 µg to 10 µg per area swiped which far exceeds the threshold limit

759 of 0.2 µg Be / 100 cm^2. All were detectable using the method developed and were in concurrence

760 with the results obtained from ICP-AES. No interference was detected when possible contaminants

761 were added to Be-spiked filters. In fact, a 100% Be recovery rate was observed from filters

762 contaminated with lubricating oil, cutting fluid and certain cleaners, the exception being Fantastic$^®$

763 spray cleaner for which a 96% Be recovery rate was observed. A comparison of results from side-

764 by-side swipe analysis highlights the accuracy of this method when compared with the ICP-AES

765 method (Fig. 2). It is difficult to compare side-by-side swipes, as they are not actually swiping the

766 exact same area but these results indicate that the fluorimetric method can stand up to even the

767 toughest test. Neither method showed consistently higher or lower biased values.

768

769   CONCLUSIONS

770   The method developed has been submitted to NIOSH for inclusion into the NIOSH Manual of

771 Analytical Methods as the standard method for the detection of beryllium on surfaces. It is a rapid

772 technique in which beryllium can be extracted from a swipe, bound to a fluorescent dye and

773 analyzed by fluorescence. We have developed the first complete system for Be detection that

774 dissolves both Be and BeO, detects Be down to 0.02 µg / swipe, tolerates a wide range of

775 interferences, and is simple to use. Our method involves placing a swipe in a dissolution solution,

776   mixing for 30 minutes, transferring a small aliquot to a detection solution and measuring the

777   fluorescence at 475 nm. The potential portability of the fluorimetric device coupled with simplicity

778   and specificity of the chemistry lends itself well to field analysis. Work is currently being carried out

779   on the integration of this method into a portable sensor platform.

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789   **Fig. 1.** Characteristic spectra for HBQS bound (475 nm) and unbound (580 nm) to Be.

790   **Table 1.** Interference Study.

791   **Table 2.** Beryllium recovery analysis from samples taken in field trials.

792   **Fig. 2.** Comparison of results obtained from side-by-side swipes including the comparison of the

793   results obtained by the fluorimetric method and the ICP analysis of the fluorimetric solution.
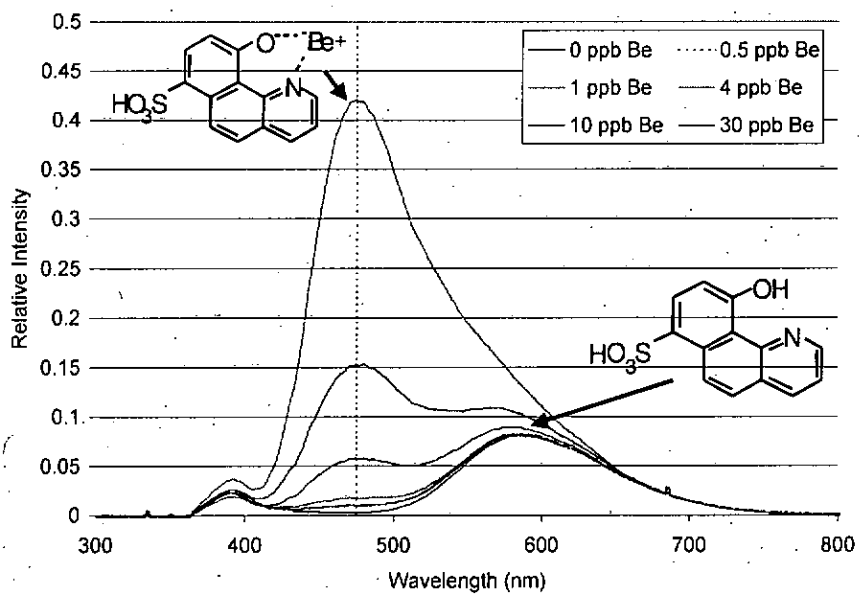
794   **Fig. 1.** Characteristic spectra for HBQS bound (475 nm) and unbound (580 nm) to Be.

795

796

797   Table 1. Interference Study.

Added Interferent	Relative Intensity at 475 nm		
	0 Be	100 nM Be	1 μM Be
No Interferent	0.005	0.112	1.078
0.4 mM Al	0.004	0.112	1.054
0.4 mM U	0.004	0.110	1.060
2.0 mM Ca	0.004	0.112	1.057
0.04 mM Li	0.004	0.112	1.060
0.4 mM Pb	0.004	0.111	1.105
0.4 mM Zn	0.003	0.112	1.103
0.4 mM Fe	0.003	0.101	0.925
0.4 mM V	0.003	0.114	1.083
0.4 mM Sn	0.003	0.113	1.105
0.4 mM W	0.003	0.116	1.103
0.4 mM Cu	0.003	0.114	1.062
0.4 mM Ni	0.004	0.114	1.074
0.4 mM Co	0.005	0.111	1.030

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825 **Table 2.** Beryllium recovery analysis from samples taken in field trials.

	Be (μg /100 cm^2)			
Sample No.	Filtrate*	Filtrate[#]	Residual on Swipe[#]	% Recovery
2003-01923				
A	0.347	0.350	ND	100
B	0.137	0.130	ND	100
C	0.134	0.120	ND	100
D	0.002	0.020	ND	100
E	5.950	6.150	0.048	99.20

F	5.425	5.400	0.052	99.05
G	5.143	5.500	0.035	99.32
H	3.179	3.210	0.047	98.54
I	6.423	6.600	0.192	97.10
J	2.182	2.030	0.034	98.46
K	4.236	4.170	0.099	97.72
L	1.137	1.050	ND	ND
M	0.007	0.020	ND	ND

826 * Measured by fluorimetric method, [#] Measured using ICP-AES, ND: Not detected

827
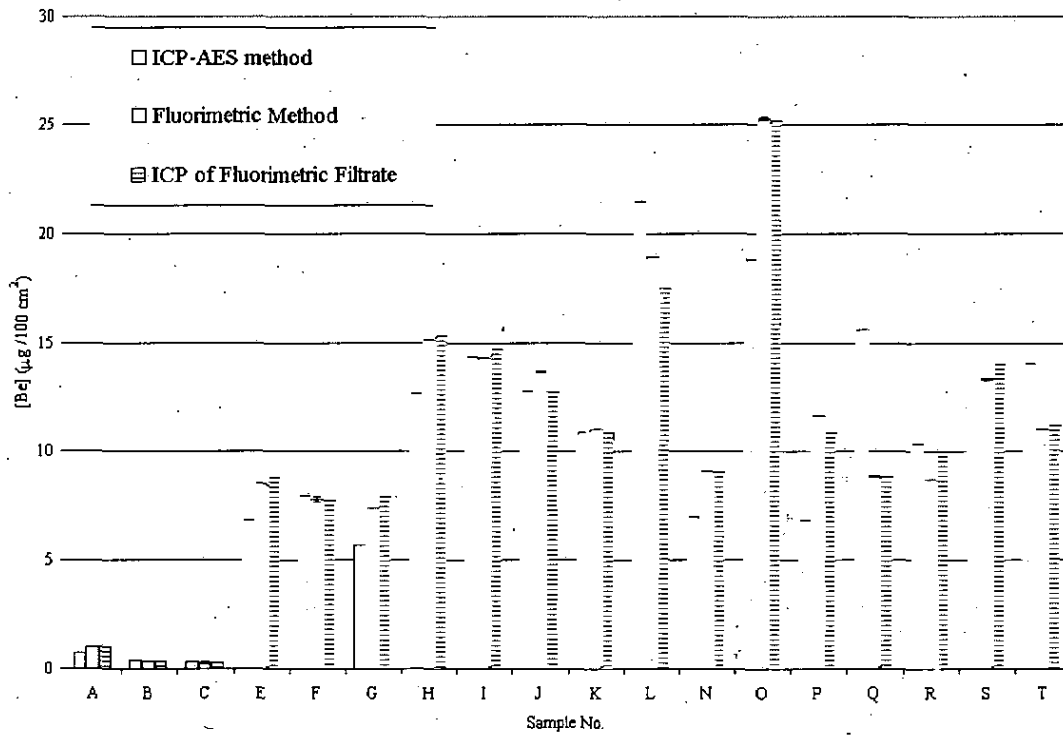
828 **Fig. 2.** Comparison of results obtained from side-by-side swipes including the comparison of the

829 results obtained by the fluorimetric method and the ICP analysis of the fluorimetric solution.

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APPENDIX 5

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836   Publication: *Interlaboratory Evaluation of a Portable Fluorescence Method for the*

837   *Measurement of Trace Beryllium in the Workplace*

Kevin Ashley,24 T. Mark McCleskey,[2] Michael J. Brisson,[3] Gordon Goodyear, [4] John Cronin[4]

and Anoop Agrawal[4]

Interlaboratory Evaluation of a Portable Fluorescence Method

for the Measurement of Trace Beryllium in the Workplace#

ABSTRACT: Researchers at Los Alamos National Laboratory (LANL) developed a field-portable fluorescence method for the measurement of trace beryllium in workplace samples such as surface dust and air filters. The technology has been privately licensed and is commercially available. In cooperation with the Analytical Subcommittee of the Beryllium Health and Safety Committee, we have carried out a

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collaborative interlaboratory evaluation of the LANL field-portable fluorescence method.

The interlaboratory study was conducted for the purpose of providing performance data that can be used to support standard methods. Mixed cellulose ester (MCE) membrane filters and Whatman 541 filters were spiked with beryllium standard solutions so that the filters spanned the range ≈0.05 – ≈0.5 µg Be per sample. Sets of these filters were then coded (to ensure blind analysis) and sent to participating laboratories, where they were analyzed. Analysis consisted of the following steps: 1. Removal of the filters from transport cassettes and placement of them into 15-mL centrifuge tubes; 2. mechanically-assisted extraction of the filters in 5 mL of 1% ammonium bifluoride solution (aqueous) for 30 minutes; 3.-4. filtration and transfer of sample extract aliquots (100 µL) into fluorescence cuvettes; 5. introduction of 1.9 mL of detection solution (to effect reaction of the fluorescence reagent with beryllium in the extracted sample); and 6. measurement of fluorescence at ≈475 nm using a portable fluorometer. This work presents performance data in support of a procedure that is targeted for publication as a National Institute for Occupational Safety and Health (NIOSH) method and as an ASTM International standard.

KEYWORDS: Beryllium, field-portable, fluorescence, interlaboratory evaluation, on-site monitoring, trace analysis, workplace

Introduction

Occupational exposure to beryllium can cause insidious and sometimes fatal disease, and new exposure limits for beryllium in air and on surfaces have been established in efforts to

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reduce exposure risks to potentially affected workers.25 Advances in sampling and analytical methods for beryllium are needed in order to meet the challenges relating to exposure assessment and risk reduction. Accurate knowledge of the level of beryllium metal present in the workplace environment is crucial for the determination of the health risks posed to workers.

Field-portable techniques for the accurate, expeditious and cost-effective monitoring of beryllium are desired to enable rapid assessment of potential worker exposures to this toxic metal in the occupational environment. These considerations have resulted in efforts to develop field-portable analytical methods for measuring trace concentrations of beryllium on-site in the workplace. Candidate techniques for beryllium field monitoring have included fluorescence26 and electroanalysis.27

In the last few years, a field-portable fluorometric method was developed by researchers at Los Alamos National Laboratory (LANL);28 this method has recently been licensed and marketed commercially.29 Owing primarily to the use of a novel fluorophore for Be^{2+} ion,30

25 Code of Federal Regulations, 10 CFR Part 850, *Chronic Beryllium Disease Prevention Program*. U.S. Department of Energy: Washington, DC (1999).

26 Ruedas Rama, M. J., Medina, A. R., Díaz, A. M., Implementation of flow-through multi-sensors with bead injection spectroscopy – fluorimetric renewable biparameter sensor for determination of beryllium and aluminum. *Talanta*, Vol. 62, pp. 879-886 (2004).

27 Wang, J., Tian, B. M., Trace measurements of beryllium by adsorptive stripping voltammetry and potentiometry. *Analytica Chimica Acta*, Vol. 270, pp. 137-141 (1992).

28 McCleskey, T. M., Presentation at the American Chemical Society national conference, Anaheim, CA (Apr. 2004).

29 Berylliant, Inc., *Manual for Procedures and Kit Description for Determination of Beryllium (BeFinder)*. Berylliant, Inc.: Tucson, AZ (Dec. 2004).

30 Matsumiya, H., Hoshino, H., Yotsuyanagi, T., A novel fluorescence reagent, 10-hydroxybenzo[*h*]quinoline-7-sulfonate, for selective determination of beryllium(II) ion at pg cm^{-3} levels. *Analyst*, Vol. 126, pp. 2082-2086 (2001).

hydroxybenzoquinoline sulfonate, the LANL field method offers significantly better limits of detection (LODs) for beryllium than were attainable by using fluorometric reagents investigated earlier. The previous methods31,32 relied on fluorescence reagents that demonstrate insufficient sensitivity for trace measurements of beryllium, which are now required in workplace settings. More recent investigations have proposed new fluorometric techniques using reagents that enable ultratrace beryllium measurement in the laboratory.[4,33]

The objective of the present study was to carry out an interlaboratory evaluation of the on-site fluorometric method for beryllium as it is currently marketed. An aim of this work was to establish estimates of method performance based on a collaborative interlaboratory analysis. These method performance parameters can then be used to support governmental methods such as those published by the National Institute for Occupational Safety and Health (NIOSH).[34] Also, it is intended that method performance data obtained through this interlaboratory trial will be used as a basis for voluntary consensus standards such as those published by ASTM International.[35]

31 Pal, B. K., Baksi, K., Chromotropic acid as fluorogenic reagent. 1. Fluorometric determination of beryllium. *Mikrochimica Acta*, Vol. 108, pp. 275-283 (1992).

32 Donascimento, D. B., Schwedt, G., Off-line and online preconcentration of trace levels of beryllium using complexing agents with atomic spectrometric and fluorometric detection. *Analytica Chimica Acta*, Vol. 283, pp. 909-915 (1993).

33 Matsumiya, H., Hoshino, H., Selective determination of beryllium(II) ion at picomole per deciliter cubed levels by kinetic differentiation mode reversed-phase high-performance liquid chromatography with fluorometric detection using 2-(2'-Hydroxyphenyl)-10-hydroxybenzo[h]quinoline as precolumn chelating reagent. *Analytical Chemistry*, Vol. 75, pp. 413-419 (2003).

34 National Institute for Occupational Safety and Health, *NIOSH Manual of Analytical Methods*, 4th ed. NIOSH: Cincinnati, OH (1994).

35 ASTM International, *Annual Book of ASTM Standards*, Vol. 11.03. ASTM International: West Conshohocken, PA (2004).

Performance Evaluation Samples

Performance evaluation material samples (PEMs) consisted of beryllium (in solution and diluted from standard beryllium nitrate solutions using deionized water) pipetted onto mixed-cellulose ester (MCE) membrane filters (Millipore, Billerica, MA) and Whatman[®] 541 cellulose fiber filters (SKC, Inc., Eighty-Four, PA). The filters were fortified at known levels between ≈0.05 and ≈0.5 µg Be per sample; the volume of the spiking aliquot was 0.1 mL. Also included were blanks of each sample medium ("spiked" with pure deionized water). After spiking by using micropipettes, the spiked filters were then allowed to dry in air at ambient temperature.

To ensure consistency with an ASTM International standard practice pertaining to interlaboratory testing,36 PEMs consisting of blanks plus sampling media spiked at four loading levels (0.050, 0.10, 0.20 and 0.40 µg Be per sample) were prepared. These PEMs were prepared with beryllium loadings targeted to bracket new action levels of 0.2 µg per 100-cm^2 sampling area for surface wipe samples[1] and 0.2 µg m^{-3} for 8-hour time-weighted average (TWA) air filter samples.37 The PEMs were prepared at a contract laboratory (Environmental Resource Associates, Arvada, CO; Lot no. 0809-04-04) under the oversight of LANL. PEMs were subsequently repackaged by the CDC/NIOSH Quality Assurance Coordinator to ensure blind analyses by the participating laboratories.

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36 ASTM E691-99, *Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method.* ASTM International: West Conshohocken, PA (1999).

37 American Conference of Governmental Industrial Hygienists, *2004 Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices.* ACGIH: Cincinnati, OH (2004); updated annually.

Interlaboratory Evaluation

Participating laboratories consisted of a subset of prospective participants that were identified by members of the Analytical Subcommittee of the Beryllium Health and Safety Committee.38 PEMs were mailed to each volunteering laboratory by the coordinating laboratory (CDC/NIOSH, Cincinnati, OH). Each participating laboratory, along with associated PEM samples, was assigned a numerical code in order to ensure anonymity.

It was requested that the participating laboratories prepare and analyze the PEMs in accordance with the marketed procedure and kit.[5] Briefly, the analysis procedure consisted of the following steps (schematized in Fig. 1):

1. Removal of the filter samples from transport cassettes and placement of them into 15-mL plastic centrifuge tubes;

2. mechanically-assisted extraction of the filters in 5 mL of 1% ammonium bifluoride solution (aqueous) for 30 minutes (in 15-mL centrifuge tubes mounted in a mechanical shaker);

3. filtration of the extracted solutions through polytetrafluorethylene (PTFE) syringe microfilters;

4. transfer of sample extract aliquots (100 µL) into fluorescence cuvettes using pipets;

5. introduction of 1.9 mL of fluorescent dye detection solution to effect reaction of the fluorescence reagent with beryllium in the extracted sample; and

6. measurement of fluorescence at ~475 nm using a portable fluorometer.

The participating laboratories were asked to report analysis results in units of mass of beryllium (in μg) per PEM sample. (This required comparison of results for unknowns with calibration standards, along with consideration of appropriate dilution and correction factors, to convert fluorescence intensity to mass.[5])
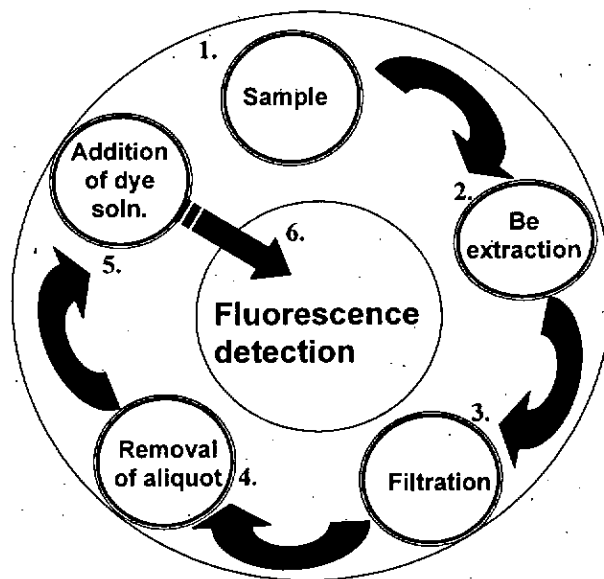

FIG. 1— Scheme for field-based preparation and fluorescence analysis of workplace samples for determination of beryllium content.

Precision, Bias and Statistical Analysis

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38 www.sandia.gov/BHSC/subs/analytical.htm (accessed 10 Dec. 2004).

ASTM International voluntary consensus standard test methods require estimates of measurement uncertainty, and this can be in the form of precision and bias data.[39] Precision estimates are preferably obtained through data from interlaboratory evaluations. Bias of a test procedure must be estimated by evaluating the performance of the test method in question against a reference method, or from determinations of recoveries from the analysis of reference material samples, or both.

In this investigation, interlaboratory precision of analytical results from the volunteer laboratories was examined using statistics from overall interlaboratory analysis results. For purposes of satisfying ASTM International standard criteria, the analysis was done using statistics described in ASTM Practice E691,[12] which requires a minimum of six participating laboratories. This standard practice also recommends a minimum of four samples for each type of matrix, with duplicate analyses of each of the four samples. Thus each laboratory received a total of ten PEM samples (five for each filter matrix) for analysis by the field-portable fluorescence method for beryllium. An analogous interlaboratory validation study has been carried out previously in order to evaluate field-portable electroanalytical procedures for on-site determination of lead in environmental samples.[40]

Repeatability and reproducibility were calculated for each of the four beryllium levels in the PEMs analyzed by the participating laboratories. Repeatability is an estimate of within-laboratory variability, while reproducibility is an estimate of the variability of both within- and

39 ASTM International, *Form and Style for ASTM Standards*. ASTM International: West Conshohocken, PA (2004).

40 Ashley, K., Song, R., Esche, C. A., Schlecht, P. C., Baron, P. A., Wise, T. J., Ultrasonic extraction and portable anodic stripping voltammetric measurement of lead in paint, dust wipes, soil and air – An interlaboratory evaluation. *Journal of Environmental Monitoring*, Vol. 1, pp. 459-464 (1999).

between-laboratory results. Repeatability was calculated by averaging the squares of the standard deviations of within-laboratory results for each beryllium level, hence the average within-laboratory variance is given by the repeatability variance, $(S_r)^2$. Reproducibility variance is expressed by:

$$(S_R)^2 = (S_r)^2 + (S_L)^2,$$

where S_L is the sample standard deviation of the mean value estimated from the average of reported interlaboratory test results for a given PEM. Relative standard deviations (RSDs) for repeatability and reproducibility (RSD_r and RSD_R, respectively) are then computed by dividing the standard deviations S_r and S_R by the mean interlaboratory test result for a particular PEM. The RSDs calculated can then be compared with the minimum precision that is desired (e.g., RSD=0.2041) for the test method under evaluation.

Estimates of analytical bias, B, were computed by simply dividing the difference between the measurand and the reference value by the reference value:

$$B = (\mu_i - R_i) / R_i.$$

Here μ_i and R_i are the mean and reference beryllium contents, respectively, for the ith beryllium loading level in each PEM sample.

Results of the Interlaboratory Evaluation

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41 ASTM E1775-01, *Standard Guide for Evaluating Performance of On-site Extraction and Portable Electrochemical or Spectrophotometric Analysis for Lead.* ASTM International: West Conshohocken, PA (2001).

Of the candidate volunteer laboratories that were identified by members of the Analytical Subcommittee of the Beryllium Health and Safety Committee, PEM filter samples were sent to eleven prospective laboratories. Analysis results were subsequently reported from eight laboratories, thereby exceeding the minimum number (for evaluation of an ASTM International test method) of six participants. Hence, for purposes of this round-robin evaluation, recruitment of a sufficient number of volunteers was achieved.

Analytical results reported by the eight individual laboratories that participated in the interlaboratory exercise are summarized in Table 1 for MCE filters and in Table 2 for Whatman 541 filters. For six of the eight laboratories, duplicate analyses were reported for PEM samples at each beryllium loading level for different sample aliquots run using (a) different portable fluorescence spectrometers or (b) different fluorescence intensity integration times, or (c) both. Overall means were computed based on the pooled means for the average of the two results reported by each laboratory for each sample (excepting the two laboratories that reported a single result). Data from blank measurements were all near to or below the reported LOD of the analytical method (≈ 0.01 µg Be per sample).[5]

Results for repeatability and reproducibility for the two PEM filter matrices, determined in accordance with ASTM E691,[12] are summarized in Table 3. Bias estimates for each PEM sample containing beryllium are presented in Table 4; overall mean values μ_i used in estimations of bias were taken from Tables 1 and 2 (for MCE and Whatman filter PEM samples, respectively).

TABLE 1—Results from measurement of beryllium content in MCE filters, as reported by

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laboratories participating in the interlaboratory evaluation. Reference values for beryllium loadings on the PEM filter samples are given in parentheses in the column headings.

Laboratory number (n=8)	Low (0.05 µg Be)	Medium low (0.10 µg Be)	Medium high (0.20 µg Be)	High (0.40 µg Be)
001	0.0512; 0.0504	0.104; 0.105	0.203; 0.207	0.468; 0.484
003	0.060; 0.050	0.11; 0.10	0.21; 0.20	0.43; 0.40
005	0.052; 0.063	0.103; 0.125	0.222; 0.273	0.459; 0.503
006	0.050	0.10	0.21	0.41
007	0.0505; 0.0490	0.103; 0.103	0.210; 0.198	0.406; 0.396
009	0.051; 0.041	0.103; 0.092	0.208; 0.199	0.421; 0.421
010	0.053; 0.053	0.104; 0.107	0.197; 0.194	0.412; 0.415
011	0.053	0.105	0.203	0.404
Overall mean ± sample standard	0.052 ±	0.10 ±	0.21 ± 0.016	0.43 ±

deviation	0.0038	0.0048		0.032
Relative Standard deviation	0.073	0.048	0.076	0.074

TABLE 2—Results from measurement of beryllium content in Whatman 541 filters, as reported by laboratories participating in the interlaboratory evaluation. Reference values for beryllium loadings on the PEM filter samples are given in parentheses in the column headings.

Laboratory number (n=8)	Low (0.05 µg Be)	Medium low (0.10 µg Be)	Medium high (0.20 µg Be)	High (0.40 µg Be)
001	0.0528; 0.0519	0.103; 0.104	0.198; 0.203	0.399; 0.406
003	0.060; 0.050	0.11; 0.10	0.22; 0.20	0.42; 0.40
005	0.055; 0.063	0.114; 0.145	0.198; 0.251	0.437; 0.492
006	0.050	0.11	0.21	0.40
007	0.0530; 0.0500	0.103; 0.099	0.203; 0.198	0.401; 0.393
009	0.056; 0.052	0.101; 0.093	0.207; 0.198	0.409; 0.410
010	0.053; 0.057	0.106; 0.104	0.205; 0.209	0.403; 0.412
011	0.056	0.104	0.207	0.409

Overall mean ± sample standard deviation	0.054 ± 0.0028	0.11 ± 0.0099	0.21 ± 0.0078	0.41 ± 0.022	
Relative standard Deviation	0.052	0.090	0.037	0.054	

TABLE 3— Repeatability and reproducibility for beryllium measurements from performance evaluation MCE and Whatman 541 filters, as computed using values reported by laboratories (n=8) participating in the interlaboratory evaluation.

Beryllium level	Average (µg Be)	S_r	S_R	RSD_r	RSD_R
MCE filters					
Low	0.052	0.0034	0.0051	0.065	0.098
Medium low	0.10	0.0052	0.0071	0.052	0.071
Medium high	0.21	0.012	0.020	0.057	0.095
High	0.43	0.0080	0.033	0.019	0.077
Whatman 541 filters					

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Low	0.054	0.0027	0.0039	0.050	0.072
Medium low	0.11	0.0068	0.012	0.062	0.11
Medium high	0.21	0.012	0.014	0.057	0.067
High	0.41	0.012	0.025	0.029	0.061

TABLE 4— Bias estimates for beryllium measurements from performance evaluation MCE and Whatman 541 filters, computed using mean values from Tables 1-3. Reference values for beryllium loadings on the filters are given in parentheses.

PEM matrix	Low	Medium low	Medium high	High
	(0.05 µg Be)	(0.10 µg Be)	(0.20 µg Be)	(0.40 µg Be)
MCE filters	0.040	0.0	0.050	0.075
Whatman 541 filters	0.080	0.10	0.050	0.025

Discussion

Results shown in Tables 1 and 2 give estimates of interlaboratory precision (as measured by the relative standard deviation, RSD) that are similar for both MCE and Whatman 541 filters. For each loading level there are no statistically significant differences between the mean beryllium contents measured in the two different sampling media (t-tests for independent means; n=8). Also, for both media (Tables 1−3), there is no apparent trend of precision changing as a

function of beryllium loading. It is noted that no outlier tests were conducted on the data which were reported by the participating laboratories: all results were included and treated statistically, despite the possibility of statistical outliers. The highest intralaboratory RSD encountered is 0.090 and all interlaboratory RSDs are 0.11 or less (Tables 1-3). Ordinarily, interlaboratory precision estimates of 0.15 and below are regarded as acceptable for PEMs such as these, that is, consisting of liquid spikes on sampling media.[16]

The results summarized in Table 3 show that figures for within-laboratory precision RSD_r spanned the range ≈ 0.02 to ≈ 0.07, while data for between-laboratory precision RSD_R were slightly greater, ranging from ≈ 0.06 to ≈ 0.11. These precision estimates compare very favorably with precision estimates from interlaboratory results for PEMs consisting of MCE filters spiked with beryllium in liquid form at similar levels (Beryllium Proficiency Analytical Testing [BePAT] program, American Industrial Hygiene Association [AIHA], 2003).[42] For AIHA BePAT PEM samples, interlaboratory RSDs of ≈ 0.06 to ≈ 0.15 (n=25) were computed from five different loading levels ranging from ≈ 0.15 to ≈ 0.6 µg Be per filter. The AIHA BePAT samples were prepared and analyzed by laboratories using reference analytical methods involving concentrated acid digestion and atomic spectrometric analysis, for example NIOSH Method 7102.[43] Thus it is shown that, for filter samples, the interlaboratory precision of the field-portable fluorescence method is at least as good as that of fixed-site laboratory methods.

42 Welch, L., Presentation at the Analytical Subcommittee meeting of the Beryllium Health and Safety Committee, Savannah River Site, SC (Feb. 2004).

43 NIOSH Method 7102, Beryllium and Compounds, as Be; in NIOSH Manual of Analytical Methods, 4th ed. NIOSH: Cincinnati, OH (1994).

Bias estimates were negligible or positive for all beryllium loadings for both PEMs (Table 4), and ranged from 0.0 to 0.10. In terms of recovery, mean values determined for beryllium loadings for all of the PEM samples (for example, see Tables 1 and 2) were within ±10% of the reference values. Typically, recoveries of 100% ±15% are regarded as acceptable for meeting the requirements of quantitative analytical methods.[44]

A limitation of this study is that this collaborative interlaboratory evaluation did not utilize real aerosol samples generated from beryllium-containing materials. Generally it is desirable to evaluate methods using performance evaluation samples that are as realistic as possible. But because of the serious health hazards and high costs associated with the generation of beryllium aerosols, it was not deemed feasible to prepare PEMs from beryllium-containing aerosols for this study. It would also be of interest to evaluate the portable fluorescence method on-site in the field, but such an effort is outside the scope of this investigation.

In summary, the results of the interlaboratory evaluation of the field-portable extraction and fluorescence method for beryllium indicate that the method is effective for the quantitative measurement of soluble forms of trace beryllium in MCE and Whatman 541 filter samples. Estimates of within-laboratory and between-laboratory precision compared favorably with interlaboratory precision estimates from a beryllium proficiency testing program, and bias estimates were 10% or below for each performance evaluation sample tested. Performance data

44 Kennedy, E. R., Fischbach, T. J., Song, R., Eller, P. M., Shulman, S. A., *Guidelines for Air Sampling and Analytical Method Development and Evaluation* (DHHS [NIOSH] Publ. No. 95-117). NIOSH: Cincinnati, OH (1995).

obtained here represent the minimum that is required for NIOSH methods and ASTM International standards. It is intended that future studies will address real-world sample matrices and on-site evaluations of the portable fluorescence method.

Disclaimer

Mention of company names or products does not constitute endorsement by the Centers for Disease Control and Prevention.

Acknowledgments

APPENDIX 6

Statistical calculations on precision and bias on Data Given in Appendix 5

Appendix 6

Precision and Bias Estimates: From Study in Appendix 5

Two matrices: MCE & Whatman 541
Four loading levels: ~0.05 „ Ÿ ~0.5 µg Be/filter   (prepared by LANL contract lab)
Media blanks included
Laboratory anonymity maintained by coding

$$(S_R)^2 = (S_r)^2 + (S_L)^2$$

S_R = reproducibility std dev
S_r = repeatability std dev
S_L = sample std dev

$$B = (\mu_j' - R_j) / R_j$$

μ_j = mean values
R_j = reference values

Results from Be-spiked MCE filters (n=8)

	Low (0.05 µg)	Med low (0.10 µg)	Med hi (0.20 µg)	High (0.40 µg)
μ_i (S$_L$)	0.052 (0.0038)	0.10 (0.0048)	0.21 (0.016)	0.43 (0.032)
RSD(%	7.3	4.8	7.6	7.4

Results from Be-spiked Whatmans (n=8)

	Low (0.05 µg)	Med low (0.10 µg)	Med hi (0.20 µg)	High (0.40 µg)
	0.054 (0.0028)	0.11 (0.0099)	0.21 (0.0078)	0.41 (0.022)
	5.2	9.0	3.7	5.4

Appendix 7

Procedure used to prepare slurry of beryllium oxide (UOX 125)*

1. Weigh out an acceptable portion of the beryllium oxide powder into a clean, tared container. We weighed approximately 3.3 mg of beryllium oxide into 100ml of DI water. After sonication for one hour to give a solution 13 micogram of beryllium/ml which was verified by ICP.

2. Wet the beryllium oxide powder with deionized water to facilitate complete transfer to the selected container.

3. Transfer the powder into the plastic or Teflon bottle. Rinse the weighing container several times, adding all rinses into the suspension standard container.

4. Dilute the suspension standard to whatever volume or mass you have chosen using only deionized water. This procedure will allow for either volumetric or gravimetric standards to be prepared. No preservative is required for the suspension standard.

5. Label the standard with sufficient information to allow for it to be used. Normalize the beryllium concentration for the beryllium oxide gravimetric factor.

6. Prior to using the standard for any serial dilutions or spiking purposes, it will need to be placed into an ultrasonic bath and sonicated for at least an hour. Sonication allows for any agglomerated particles to be dispersed and well mixed in the standard. Failure to sonicate the suspension may result in standards that do not support accurate serial dilutions or spiking. Sonication is needed on the day of use for the suspension standard.

Hand shaking can be employed to mix the sonicated standard during the day, if it needs to be used repetitively.

7. Following these steps should allow for the suspension standard to be used as a primary standard for the preparation of serial dilutions of the standard to best approximate levels commonly seen in each individual lab.

* Developed by Dr. Tom Oats, Oak Ridge National Laboratory.